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MATHÉMATIQUES

SUR LA RÉSOLUBILITÉ ET LA STABILITÉ DU PROBLÈME DE DIRICHLET

Par M. KELDYCH

(Présenté par I. M. Vinogradow de l'Académie, le 29. XII. 1937)

Je me propose d'indiquer dans cette note certains résultats concernant la résolubilité et la stabilité du problème de Dirichlet ainsi que la représentation des fonctions par des séries uniformément convergentes de polynômes harmoniques. J'exposerai les résultats pour l'espace à trois dimensions, mais ils restent valables pour un nombre de dimensions plus grand.

§ 1. Résolubilité du problème de Dirichlet. Soit D un domaine arbitraire, $\sum$ — sa frontière, $d_1, d_2, \ldots, d_n, \ldots$ — une suite de domaines bornés par des surfaces analytiques $s_1, s_2 \ldots, s_n, \ldots$ telles que $\bar{d}_n = d_n + s_n$ est contenu dans D et que les domaines d_n convergent vers D de telle manière que chaque ensemble fermé appartenant à D appartient à d_n à partir d'une certaine valeur de n. Soit $f(P)$ une fonction continue sur $\sum$, $\varphi(P)$ — une fonction continue dans tout l'espace et coïncidant avec $f(P)$ sur $\sum$. En suivant Wiener [1] nous allons considérer la suite des fonctions:

$$u_{1,\varphi}(P),\ u_{2,\varphi}(P), \ldots, u_{n,\varphi}(P), \ldots,$$

où $u_{n,\varphi}$ est définie dans d_n et coïncide avec $\varphi(P)$ sur s_n. Soit $u_f(P)$ la limite de $u_{n,\varphi}(P)$ dans D. La fonction $u_f(P)$ est nommée solution généralisée du problème de Dirichlet pour le cas où la fonction donnée $f(P)$ est bornée.

Nous dirons que le problème de Dirichlet pour une $f(P)$ donnée est résoluble en un point frontière Q, si $\lim\limits_{P \to Q} u_f(P) = f(Q)$.

Soit Q un point quelconque de $\sum$, on a le

Théorème 1. *Si* $P \to Q$, *alors ou bien toutes les valeurs limites* $uf(P)$ *sont au plus égales à* $f(Q)$, ou bien toutes les valeurs limites $uf(P)$ sont au moins égales à $f(Q)$.

Soit $\omega(Q, f)$ l'oscillation * de la fonction $u_f(P)$ au point Q. Il suit du théorème 1

Théorème 2. *L'oscillation* $\omega(Q, f)$ *est une fonctionnelle linéaire de* $f(P)$. Cette fonctionnelle peut être représentée dans la forme:

$$\omega(Q, f) = \int_{\Sigma} [f(P) - f(Q)]\, d\omega_Q,$$

* On considère $\omega(Q, f)$ comme positif si les valeurs limites $U_\varphi(P)$ sont au moins égales à $f(Q)$, dans le cas contraire il est considéré comme négatif.

où $\omega_Q(e)$ est une fonction positive, continue et additive de l'ensemble e, $e \subset \sum$. Il suit des résultats indiqués qu'il existe une infinité dénombrable de points irréguliers de $\sum$, $Q_1, Q_2, \ldots, Q_n \ldots$, tels que si le problème de Dirichlet pour la fonction donnée $f(P)$ est résoluble aux points de cet ensemble, il est résoluble pour une $f(P)$ donnée dans tout le domaine D. Les conditions de résolubilité dans D peuvent être présentées dans la forme:

$$\int_{\sum} [f(P) - f(Q_n)]\, d\omega_{Q_n} = 0, \quad (n = 1, 2, \ldots).$$

§ 2. Stabilité du problème de Dirichlet. Soit D un domaine simplement connexe, dont la frontière $\sum$ est la frontière du domaine D_∞, contenant le point à l'infini. Considérons une suite de domaines simplement connexes $D_1, D_2, \ldots, D_n, \ldots$ bornés par des surfaces analytiques $S_1, S_2, \ldots, S_n, \ldots$, et tels que $D_n \supset \overline{D} = D + \sum$, et les D_n convergent vers D, c'est-à-dire chaque ensemble fermé appartenant à D_∞, à partir d'un certain n, est situé hors de D_n. Soient $f(P)$ et $\varphi(P)$ les fonctions définies dans le § 1. Considérons la suite des fonctions:

$$U_{1,\varphi}(P), U_{2,\varphi}(P), \ldots, U_{n,\varphi}(P), \ldots,$$

la fonction $U_{n,\varphi}(P)$ étant harmonique dans D_n et coïncidant avec $\varphi(P)$ sur S_n. Les fonctions $U_{n,\varphi}$ convergent vers $\overline{D}$, et la convergence est uniforme à l'intérieur de D. Soit $U_f(P)$ la fonction limite. Nous dirons que le problème de Dirichlet pour la fonction donnée $f(P)$ est stable à l'intérieur du domaine D, si aux points de D on a $D - U_f(P) = u_f(P)$. Le problème de Dirichlet est stable dans le domaine fermé $\overline{D}$, si les fonctions $U_{n,\varphi}(P)$ convergent uniformément vers $f(P)$ sur $\sum$. Le problème de Dirichlet pour une $f(P)$ donnée est stable au point frontière Q, si $U_f(Q) = f(Q)$. Si cette égalité a lieu pour une fonction continue $f(P)$ quelconque, le point Q est nommé point de stabilité *. Remarquons tout de suite que, si le problème de Dirichlet est stable dans un domaine fermé, il est résoluble dans ce domaine.

Stabilité en un point frontière. Signalons d'abord la propriété suivante de la fonction $U_f(P)$.

Théorème 3. *Soit Q un point frontière de D. Si $P \to Q$, toutes les valeurs limites de la fonction $U_f(P)$ sont comprises entre $U_f(Q)$ et $f(Q)$.*

En désignant par $\Omega(Q, f)$ l'oscillation de la fonction $U_f(Q)$ au point Q, on a:

Théorème 4. *L'oscillation $\Omega(Q, f)$ est une fonctionnelle linéaire de $f(P)$.* Cette fonctionnelle peut être représentée dans la forme:

$$\Omega(Q, f) = \int_{\sum} [f(P) - f(Q)]\, d\Omega_Q,$$

où $\Omega_Q(e)$ est une fonction d'ensemble e, $e \subset \sum$, positive, continue et additive.

Chaque point de stabilité de $\sum$ est en même temps un point régulier. On a le critère suivant pour les points de stabilité.

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* Ces définitions ont été données et étudiées par M. Lavrentieff et l'auteur pour les domaines dont la frontière est une courbe de Jordan [2]; mais la méthode précédemment employée était essentiellement basée sur l'hypothèse que la frontière est une courbe jordanienne.

Théorème 5. *Soit Q un point frontière de D, λ_n — la capacité intérieure* (2) *de l'ensemble des points de D_∞, dont la distance à Q est comprise entre 2^{1-n} et 2^{-n}.* Le point Q est un point de stabilité ou ne l'est pas, suivant que la série $\sum 2^n \lambda_n$ est divergente ou bien convergente.

Stabilité dans un domaine. Les théorèmes suivants rattachent la stabilité du problème de Dirichlet dans un domaine avec la stabilité aux points frontières.

Théorème 6. *Afin que le problème de Dirichlet pour une $f(P)$ donnée soit stable à l'intérieur d'un domaine, il est nécessaire et suffisant qu'il soit stable en tous les points de la frontière, sauf peut-être les points d'un ensemble de mesure harmonique nulle.*

Théorème 7. *Si le problème de Dirichlet est résoluble dans D et stable à l'intérieur de D, il est stable dans le domaine fermé $\overline{D}$. Si le problème de Dirichlet est stable à l'intérieur de D et résoluble en un point frontière Q, il est stable en Q.*

Théorème 8. *Si le problème de Dirichlet est stable en chaque point de $\sum$, il est stable dans le domaine fermé.*

Théorème 9. *Il existe un ensemble dénombrable de points $Q_1, Q_2, \ldots$ $\ldots, Q_n, \ldots$, tels que, pour la stabilité du problème de Dirichlet, pour une $f(P)$ donnée, dans le domaine $\overline{D}$, il est nécessaire et suffisant que les inégalités:*

$$\int_{\sum} [f P) - f(Q_n)]\, d\Omega_{Q_n} = 0 \qquad (n = 1, 2, \ldots)$$

aient lieu.

Domaines de stabilité. Nous allons donner maintenant quelques propositions qui caractérisent les classes de domaines pour lesquels chaque problème de Dirichlet est stable.

Théorème 10. *Pour que chaque problème de Dirichlet soit stable dans un domaine fermé $\overline{D}$, il est nécessaire et suffisant que chaque point de $\sum$ soit un point de stabilité.*

Théorème 11. *Pour que chaque problème de Dirichlet soit stable à l'intérieur de D, il est nécessaire et suffisant que l'ensemble de points de non stabilité soit de mesure harmonique nulle.*

Il suit du théorème 7 que pour les domaines de cette nature chaque point régulier est un point de stabilité.

Théorème 12. *Pour que le problème de Dirichlet soit stable dans $\overline{D}$, quels que soient les données frontières pour lesquelles il est résoluble, il faut et il suffit que l'ensemble de points réguliers de $\sum$ coïncide avec l'ensemble de points de stabilité.*

Nous remarquerons ici que dans le cas d'une frontière $\sum$ jordannienne les théorèmes 5, 7, 10 et 11 ont été déjà obtenus par M. Lavrentieff et l'auteur (2). Dans le présent travail on donne un exemple d'un domaine pour lequel le problème de Dirichlet est résoluble, mais il peut être instable à l'intérieur de ce domaine.

§ 3. Représentation des fonctions par des séries de polynômes harmoniques. La question de la stabilité du problème de Dirichlet se rattache étroitement à l'étude de la représentation des fonctions par des séries de polynômes harmoniques sur un continu. Soit F un continu, $f(P)$ — une fonction définie sur F et qui est représentable sur F par une série de polynômes uniformément convergente. Alors $f(P)$ doit être continue sur F et harmonique aux points intérieurs de F. Signalons la proposition suivante.

Théorème 13. *Soit F un continu, P — un point frontière de F, $\lambda_n(P)$ — la capacité intérieure de l'ensemble de points de O_n, complémentaire de F, dont la distance à F est comprise entre 2^{1-n} et 2^{-n}, $\gamma_n(P)$ — la capacité de O_n. Pour que chaque fonction $f(P)$ continue sur F soit représentable par une série de polynomes harmoniques convergeant uniformément sur F, il faut et il suffit que* 1) *le continu F ne morcelle pas l'espace*; 2) *les séries $\sum 2^n \gamma_n(P)$, $\sum 2^n \lambda_n(P)$ soient simultanément convergentes ou divergentes en chaque point frontière de F.*

Signalons encore la proposition suivante:

Théorème 14. *Il existe un continu partout non dense qui ne morcelle pas l'espace et qui jouit de la propriété suivante:*

Si deux fonctions U et V, représentables sur F par des séries uniformément convergentes de polynomes harmoniques, coïncident sur une certaine portion de F, elles coïncident sur tout le continu F.

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MATHÉMATIQUES

SUR LA DÉFORMATION DES CONGRUENCES RECTILIGNES AVEC CONSERVATION DES SURFACES RÉGLÉES PRINCIPALES

Par S. ROSSINSKI

(Présenté par S. Tschapliguine, de l'Académie, le 25. XII. 1937)

§ 1. Considérons une surface quelconque S et une congruence rectiligne C. Supposons les rayons de C invariablement liés aux plans tangents correspondants de la surface S.

Lorsqu'on déforme S d'une façon quelconque, les différents rayons de la congruence C entraînés dans la déformation, ne cessent de constituer une congruence qui s'appelle déformée de l'initiale.

Si au cours de cette déformation les surfaces réglées principales de la congruence C restent invariables, on dit qu'il s'agit d'une déformation avec conservation des surfaces réglées principales.

Le problème indiqué n'est pas encore résolu dans le cas d'une position arbitraire du rayon de la congruence par rapport au plan tangent correspondant.

J'ai déjà étudié (1) le cas d'une congruence C dont les rayons sont orthogonaux aux plans tangents correspondants de la surface S.

La présente note a pour objet l'étude des congruences C dont les rayons restent dans les plans tangents correspondants au cours de la déformation de la surface S.

Le cas d'une déformation arbitraire de la surface S est privé de résultats intéressants. Dans tout ce qui suit il s'agit de la déformation continue de la surface S à réseau conjugué persistant, c'est-à-dire, de la déformation à base principale.

§ 2. Supposons que la surface S soit douée d'une base principale et rapportée à cette base. Soient $\bar{\rho}(u, v)$, $\bar{n}(u, v)$ le vecteur définissant S et le vecteur unitaire de sa normale. Désignons par $E, F, G, D, D'=0, D''$ les coefficients des formes $d\bar{\rho}^2$ et $-d\bar{\rho}d\bar{n}$ attachées à S. Soit, enfin, l la longueur du segment porté sur le rayon de la congruence par les tangentes aux courbes coordonnées (u, v) et $\bar{\zeta}$ le vecteur unitaire définissant ce rayon-même.

Alors on a:

$$\bar{\zeta} = \frac{1}{l}\left(\frac{\eta\bar{\rho}_v}{\sqrt{G}} - \frac{\xi\bar{\rho}_u}{\sqrt{E}}\right) = a\bar{\rho}_u + b\bar{\rho}_v,$$

où la signification géométrique des valeurs ξ et η est facile à comprendre.

Supposons que la surface de départ de la congruence C est définie par le vecteur:

$$\bar{\rho}_1 = \bar{\rho} + \frac{\xi\rho_u}{\sqrt{E}} = \bar{\rho} + c\bar{\rho}_u.$$

Soient

$$d\bar{\zeta}^2 = E_0 du^2 + 2F_0 du dv + G_0 dv^2$$

et

$$d\bar{\zeta}\, d\bar{\rho}_1 = e du^2 + (f + f')\, du dv + g dv^2$$

deux formes fondamentales de Kummer attachées à la congruence C.

L'équation différentielle des surfaces réglées principales de C

$$\begin{vmatrix} E_0\, du + F_0 dv, & F_0\, du + G_0\, dv, \\ 2e\, du + (f + f')\, dv, & (f + f)\, du + 2g\, dv \end{vmatrix} = 0,$$

en tenant compte de l'équation de Gauss $DD'' = KH^2$ (K—courbure de S, $H^2 = EG - F^2$), prend la forme suivante:

$$D^4(\lambda du^2 + 2\mu\, du\, dv) + D^2(\lambda_1 du^2 + 2\mu_1 du\, dv + \nu_1 dv^2) + \\ + 2\mu_2 du\, dv + \nu_2 dv^2 = 0,$$

où, ayant posé $m = f + f'$, $n = F_0$, on a:

$$\left.\begin{array}{ll} \lambda = a(am - 2cn); & \mu_1 = gM - PQ - ab^2cK^2H^4; \\ \mu = a(ag - cQ); & \nu_1 = 2gn - Qm; \\ \lambda_1 = Mm - 2Pn; & \mu_2 = Pb^2K^2H^4;\ \nu_2 = mb^2k^2H^4, \end{array}\right\} \quad (1)$$

où P, Q et M sont des fonctions déterminées par rapport aux E, F, G, a, b et leurs dérivées du premier ordre.

Les trois équations suivantes:

$$\left.\begin{array}{l} \lambda\, du^2 + 2\mu\, du\, dv = 0, \\ \lambda_1 du^2 + 2\mu_1 du\, dv + \nu_1 dv^2 = 0, \\ 2\mu_2 du\, dv + \nu_2 dv^2 = 0, \end{array}\right\} \quad (2)$$

doivent évidemment se réduire à une seule pour le problème en considération.

Écartons le cas des surfaces réglées principales confondues, qui ne peut donner que des congruences dégénérées. On peut alors signaler par rapport aux coefficients des équations (2) cinq hypothèses suivantes:

1) $\lambda = \mu = \lambda_1 = \mu_1 = \nu_1 = \mu_2 = \nu_2 = 0$;
2) $\lambda = \lambda_1 = \nu_1 = \nu_2 = 0$;
3) $\lambda = \mu = \lambda_1 = 0$; $\mu_1 : \mu_2 = \nu_1 : \nu_2$;
4) $\nu_2 = \mu_2 = \nu_1 = 0$; $\lambda : \lambda_1 = \mu : \mu_1$;
5) $\lambda = \mu = \mu_2 = \nu_2 = 0$.

§ 3. Considérons d'abord deux cas particuliers.

I. Soit $a = -\dfrac{\xi}{l\sqrt{E}} = 0$. Dans ce cas on peut prendre $l = \eta = \infty$, $\xi \neq 0$. Le cas où l'on a $\xi = 0$ est un cas particulier de celui-ci. Alors, ξ étant différent de zéro, on trouve que la surface S doit être une surface arbitraire douée d'une base principale (u, v).

Si sur la tangente de la courbe $v = \text{const.}$, à partir du point de contact, on porte un segment ξ défini par l'équation:

$$\left\{\begin{matrix} 12 \\ 1 \end{matrix}\right\}\left(\xi_v - \xi \left\{\begin{matrix} 12 \\ 2 \end{matrix}\right\}\frac{F}{E}\right) - \left\{\begin{matrix} 22 \\ 1 \end{matrix}\right\}\left(\sqrt{E} + \xi_u - \xi \left\{\begin{matrix} 11 \\ 2 \end{matrix}\right\}\frac{F}{E}\right) + \xi GK = 0, \quad (3)$$

et si l'on mène par son extrémité une droite parallèle à la tangente de la courbe $u = \text{const.}$ de la base principale, on obtient le rayon de la congruence cherchée. Il est aisé de voir que, si les segments ξ_1 et ξ_2 définissent les congruences cherchées, le segment $\xi = \dfrac{\xi_1 + p\xi_2}{1 + p}$, p étant une constante, fournit lui aussi une solution du problème posé.

La congruence C peut se réduire à une congruence de normales seulement à condition $\xi = 0$; par suite, en vertu de l'équation (3), on a $\left\{\begin{matrix}22\\1\end{matrix}\right\} = 0$. Ainsi, C étant une congruence de normales, les seules solutions du problème posé, sont les surfaces S douées d'une base principale comprenant une famille de géodésiques (u=const). Les rayons de la congruence C de normales sont des tangentes de cette famille de géodésiques.

II. Soit maintenant $b = 0$. C'est un cas géométriquement équivalent au cas $\xi = 0$ considéré tout à l'heure.

§ 4. L'étude des 5 cas signalés au § 2 montre que c'est uniquement le cas 2) qui présente un intérêt, car tous les autres cas se réduisent au cas 1); or, C étant une congruence isotrope, ce dérnier cas est un cas banal pour le problème posé.

Quant au cas 2) les formules (1) montrent que dans ce cas nous arrivons seulement à deux conditions suivantes: $m = 0$, $n = 0$.

Ces équations et les trois équations bien connues que doivent vérifier les coefficients E, F, G d'un ds^2 donné pour que les courbes coordonnées forment une base principale sur ∞^1 surfaces représentatives [2], nous déterminent les segments ξ et η coupés sur les tangentes aux courbes coordonnées par le rayon de la congruence.

Ainsi, une surface S arbitraire douée d'une base principale se présente comme une solution du problème posé.

Si l'on exige que C soit une congruence de normales, on trouve que cela peut arriver seulement dans les cas déjà signalés $a = 0$, $b = 0$.

La méthode employée ne permet pas d'étudier le cas d'un rayon passant par le point de contact du plan tangent correspondant et différant des tangentes aux courbes de la base principale. Ce cas attend encore sa solution.

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MATHEMATICS

OSCILLATION THEOREMS FOR THE DIFFERENTIAL BOUNDARY VALUE PROBLEMS OF THE FOURTH ORDER

By D. SHIN

(Communicated by S. N. Bernstein, Member of the Academy, 6.I.1938)

Consider the self-adjoint differential system of the fourth order

$$P\frac{d}{ax}y^{[3]} + Ry^{[2]} + (\psi - \lambda\tau)y^{[0]} = 0, \quad (a \leqslant x \leqslant b, \quad -\infty < \lambda < \infty), \quad (1)$$

$$\sum_{\nu=1}^{4} \alpha_{k\nu} y_{(a)}^{[4-\nu]} + \sum_{\nu=1}^{4} b_{k\nu} y_{(b)}^{[4-\nu]} = 0 \quad (k = 1-4) \quad (2)$$

where

$$y^{[0]} = py,\ y^{[1]} = q\frac{d}{ax}y^{[0]},\ y^{[2]} = \rho\frac{d}{ax}y^{[1]} + \sigma y^{[0]},\ y^{[3]} = q\frac{d}{ax}y^{[2]} + \varphi y^{[1]},\ R = \frac{p\sigma}{\rho};$$

the functions $p(x) > 0$, $q(x) > 0$, $\rho(x) > 0$, $\sigma(x) \leqslant 0$, $\varphi(x) \leqslant 0$, $\psi(x)$ and $\tau(x) > 0$ are real and continuous on a finite closed interval (a, b). The boundary conditions (2) either can be written as

$$y_{(a)}^{[k]} = \sum_{j=0}^{3} h_{kj} y_{(b)}^{[3-j]},\ y_{(b)}^{[k]} = \sum_{j=0}^{3} (-1)^{k+j+1} h_{jk} y_{(a)}^{[3-j]} \quad (k = 0-3);$$

or, at least, two of them can be reduced to

$$\sum_{j=0}^{3} (-1)^j a_j y_{(a)}^{[j]} = 0,\ \sum_{j=0}^{3} b_j y_{(b)}^{[j]} = 0.$$

According to professor S. A. Janczewsky (1), we call the boundary conditions (2) regular, if the constants h_{kj} or $a_j(b_j)$ have the same sign. It is easy to show that if at any point $x_0, a \leqslant x_0 < b$, we have $y_{(x_0)}^{[k]} \geqslant 0$ (or $\leqslant 0$), $k = 0-3$, then it must be $y_{(x)}^{[k]} > 0$ (or < 0), $k = 0-3$ on $x_0 < x \leqslant b$; and if at any point $x_0, a < x_0 \leqslant b$, we have $(-1)^k y_{(x_0)}^{[k]} \geqslant 0$ (or $\leqslant 0$), $k = 0-3$, then it must be $(-1)^k y_{(x)}^{[k]} > 0$ (or < 0), $k = 0-3$, on $a \leqslant x < x_0$. It follows from the conditions of regularity of (2) that all the characteristic values λ which satisfy the condition $\psi(x) - \lambda\tau(x) < 0$ on (a, b), are of index 1 or 2, and the fundamental functions corresponding to them have only simple roots in (a, b). The number m of the irregular characteristic values is finite. For instance, if $\psi(x) = 0$ then $m \leqslant 7$.

In the cese when the boundari conditions (2) are reduced to the Sturm's type, that is, when two of them refer to one end of (a, b) and the other two refer to the second end of (a, b), all the regular characteristic values are of index 1 and they are arranged as follows

$$\lambda_{m+1} < \lambda_{m+2} < \lambda_{m+3} < \lambda_{m+4} < \cdots$$

In the general case they are arranged either as

$$\lambda_{m+1} \leqslant \lambda_{m+2} < \lambda_{m+3} \leqslant \lambda_{m+4} < \cdots;$$

or as

$$\lambda_{m+1} < \lambda_{m+2} \leqslant \lambda_{m+3} < \lambda_{m+4} \leqslant \cdots$$

In the Sturm's case the fundamental function $y_n(x, \lambda_n)$, $n \geqslant m+1$, has either $n-2$ or $n-1$ or n roots on (a, b); and in the generel case the fundamental functions $y_{n-1}(x, \lambda_{n-1})$, $y_n(x, \lambda_n)$, $y_{n+1}(x, \lambda_{n+1})$, $n-1 \geqslant \geqslant m+1$, have either $n-3$ or $n-2$ or $n-1$ or n or $n+1$ roots in (a, b), independently from one another.

If we consider the different canonical forms of boundary conditions, the oscillation theorems can be defined more accurately, just as they have been established by professor S. A. Janczewsky for the differential system

$$\frac{d^2}{dx^2}\left(\rho(x)\frac{d^2y}{dx^2}\right) + (\psi(x) - \lambda\tau(x))\,y = 0,$$

$$\sum_{\nu=1}^{4} a_{k\nu} y_{(a)}^{(4-\nu)} + \sum_{\nu=1}^{4} b_{k\nu} y_{(b)}^{(4-\nu)} = 0, \quad k = 1-4.$$

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PHYSICS

ON MAGNETIC ANISOTROPY IN FERROMAGNETIC CRYSTALS IN WEAK FIELDS

By E. KONDORSKY

(Communicated by S. I. Wawilow, Member of the Academy, 12. I. 1938)

The «Physical Review» has recently published important results of Williams (1) who first studied the magnetic properties of crystals in specimens of closed form. Williams showed that the magnetization curves of crystals are different along different directions even in weak fields. The initial magnetic susceptibilities along the [100], [110] and [111] directions were found to be approximately in the ratio of 6 : 3 : 2.

The fact that magnetic anisotropy may exist even in weak fields was first indicated by Akulov (2). Akulov came to this conclusion having assumed that the work expended on magnetization in any direction is one and the same function of the sum of the components of the magnetization vector along the axes of easy magnetization. From this Akulov found that in weak fields the values of the susceptibilities along the [100], [110] and [111] axes should be in the ratio of 6 : 3 : 2.

To explain magnetic anisotropy in weak fields Bosorth (3) has assumed that when H is applied, for example, along the [110] direction the component of H along [100] will produce a magnetization in that direction given by the [100] magnetization curves. On the basis of this assumption Bosorth comes to the conclusion that the initial susceptibility along the [100], [110] and [111] axes should be also as 6 : 3 : 2.

It should be noticed that both these conclusions inevitably contain certain implicit assumptions concerning the initial state of the crystal before magnetization. The question is worthy to be examined from the viewpoint of a model of the process of magnetization in weak fields, considered as a process of displacement of boundaries between regions of spontaneous magnetization. The model has had its origin in the works of Sixtus and Tonks (4) and has been developed theoretically by Becker (5) and Bloch (6), and in part in the writers recent work too (7). Starting with this model we find that in weak fields when the spin remains directed along the axes of easy magnetization, the susceptibility of iron may be divided into two parts *: $\chi_{\parallel} = \frac{I_{\parallel}}{H}$ and $\chi_{\perp} = \frac{I_{\perp}}{H}$ where I is the

* It should be noticed that in his work Akulov (2) also divided the magnetization into two parts, the first, initial, being the magnetization arising from longitudinal inversions of spins, and the second from transverse ones, but this author considered the process of inversion of spins from a quite different point of view.

magnetization arisiog from the displacement of boundaries between regions with anti-parallel resultant spins; and $I_\perp$ is the magnetization arising from the displacement of boundaries between regions with resultant spins forming an angle of 90°. To obtain the formula for magnetic anisotropy in weak fields it was necessary to calculate $\chi_\parallel$ and $\chi_\perp$ for arbitrary directions in the crystal. The result of those calculations * was the following general formula of the initial crystal susceptibility χ_0 which is valid for an arbitrary distribution of spins previous to magnetization and an arbitrary directed magnetization:

$$\left.\begin{aligned} \chi_0 &= \chi_\parallel + \chi_\perp \\ \chi_\parallel &= \chi_1(n_1 h_1^2 + n_2 h_2^2 + n_2 h_3^2), \\ \chi_\perp &= \chi_2[n_1 n_2(h_1^2 + h_2^2) + n_2 n_3(h_2^2 + h_3^2) + n_3 n_1(h_3^2 + h_1^2)], \end{aligned}\right\} \qquad (1)$$

where n_1, n_2, n_3 (given by fractions) are the parts of unit volume of the crystals in which the spins are parallel or anti-parallel to the axes of easy magnetization [100], [010] and [001] respectively: in other words, n_1, n_2, n_3 are the concentrations of the different magnetic phases, h_1, h_2, h_3 are the cosines of the angles between the directions of the magnetic field and the axes; χ_1 and χ_2 are coefficients independent of the direction of magnetization, provided that in any one direction of easy magnetization the magnitudes of the stress-gradients, and their spatial distribution, are on an average the same as in any other.

It follows from (1) that if there is uniform distribution of the spins, i. e. if $n_1 = n_2 = n_3$, the susceptibility should not depend on the direction of the field. Thus the presence of magnetic anisotropy in Williams' crystals should, from the viewpoint of the model under consideration, be explained as a result of the presence of preferential spin orientations. From the calculations of Kaya and Takaki ([8]), made on the basis of measurements of magnetostriction in crystals of iron, it follows that, in the initial condition, the spins are preferentially orientated along these directions of easy magnetization for which the demagnetizing factor has the least value in a specimen of the given form. From this it follows that in Williams' specimens, the values of n_1, n_2, n_3 could hardly be equal to one another. It is very probable that in specimens cut along the direction [100] the greater part of the spins were orientated parallel or anti-parallel to this direction, particularly after the specimen had been magnetized once. If it happens that for $H_\parallel$ [100] we have $n_1 = 1$, $n_2 = n_3 = 0$; for $H \parallel$ [110], $n_1 = n_2 = \frac{1}{2}$, $n_3 = 0$ and for $H \parallel$ [111], $n_1 = n_2 = n_2 = \frac{1}{3}$, i. e. if there is a most preferential orientation it follows from (1) that the initial susceptibilities in these cases should be as $6 : 3 + \frac{3}{2}\frac{\chi_2}{\chi_1} : 2 + \frac{4}{3}\frac{\chi_2}{\chi_1}$, when $\chi_2 \ll \chi_1$ this gives the ratio 6 : 3 : 2.

There is reason to suppose that $I_\parallel$ is either entirely, or to a considerable degree irreversible. If this is a matter of fact, the initial reverible susceptibility of Williams' crystal in the [100] direction must be small compared to the irreversible part of initial susceptibility (up to the present time the initial susceptibility has been supposed equal to the

* The calculation of $\chi_\parallel$ was produced on basis of formulas (7) and (8) of previous paper ([7]). The calculation oj $\chi_\perp$ was produced in general by the same way as the calculation carried out by Becker ([5]) for the case when magnetic field is parallel to any one of the directions of easy magnetization, and the spins are equally distributed among these directions (Becker considered in his calculation two directions of easy magnetization perpendicular to one another).

initial reversible susceptibility). Therefore, measurements of the reversible susceptibility of these crystals would be of interest.

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CHEMICAL PHYSICS

THE SYNTHESIS OF NITRIC OXIDE IN THE TORCH DISCHARGE

By K. N. MOTCHALOFF

(Communicated by N. N. Semenov, Member of the Academy, 14. XII. 1937)

At ultra high frequencies of the order 10^8—10^7 Hz, a new type of discharge is observed. It was first described in 1928 by S. I. Zilitinkevitsh (1) who called it «torch effluvium». It has the form of a narrow gas flame (Zilitinkevitsh had it in the shape of a pear) and may be caused to appear at the places of tension inflation in the oscillatory circuit or Lecher system connected with a generator.

Its dimensions depend on the power and tension applied, reaching, for instance, a hight of 15 cm at a power of 200 W. The torch itself emits a weak light of a light blue colour, like that of the discharges obtained in vacuum tubes.

Three zones may be easily distinguished in it: 1) the largest one in the middle is of a light blue colour; 2) the narrow inner one of a considerably lighter colour, forming, as it were, the axis of the torch; 3) the outside covering, of a brownish-yellow colour, develops at the top into a very mobile tail of the same colour.

The scheme of the apparatus we used to obtain this phenomenon is represented in Fig. 1.

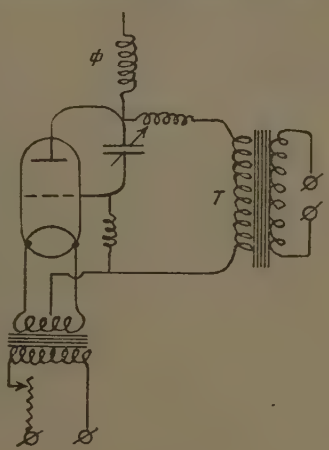

Fig. 1.

The voltage 4000 V was transferred to the anode directly from the transformator T, the plant working thus at one half-period. The glow current and the anode voltage were kept up constant by means of rheostates in the primary circuits of respective transformators.

Coil F at the end of which the torch discharge was generated was correspondingly tuned through extending or approaching its rounds.

The wave length measured according to the Lecher system, was 720 cm in all the tests.

The «temperature» of the torch if meant in the usual sense seems to be considerably lower than in the voltaic arc, but not below 2000° C. When electrodes of metals with a poor heat conductibility (Fe, Pt,...) are used we generally can observe their tips to become white-glowing and sometimes melt-

ing around. If made of silver, an intensive pulverization of the latter is observed.

The mechanism of this phenomenon, the electrical and thermal conditions inside the torch and, more particularly, the chemical processes taking place there are still unknown.

We are therefore unable to compare this kind of discharge with the types already known. The high temperature and pressure (atmospheric), as well as the outward aspect of the torch make it similar to the arc. It differs, however, from the latter in that it «burns» on one electrode (without any participation of the other) as well as on account of the electric field in it being most peculiar. The volume density of the energy in it is much greater than in the electric arc, because at a power of 100 W, for instance, the torch reaches a length of more than 6 cm, whereas the arc is but 1 cm long (at about equal sections). Hence we have to expect a much lower temperature what is confirmed by the experiment.

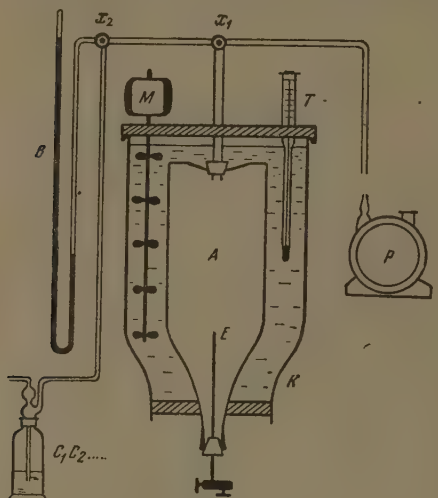

Fig. 2.

From the purely chemical standpoint the torch discharge should be of great interest, as we find conveniently combined in it a high frequency rate and not too great volume density of energy with the possibility to work at high concentrations (atmospheric pressure) of the reacting gases. This may be expected to have a favourable influence on the synthesis of nitric oxide the energetic yield of which is steadily increasing with frequency, as Ch. H. Wakker and B. Briner (2), E. Briner, Ch. H. Wakker (3) and others have shown. The works concerned with the oxydation of nitrogen made evident that this process does not require a very high macro-temperature, as it was accomplished by Warburg, Leithauser (4), Berthelot (5) and others in a dark discharge. Haber and his collaborators(6) maintain that in the arc discharge also the primary effect is an electric one and that it is the more marked, the lower the temperature of the arc. The most essential points for judging of the practical value of the synthesis of NO in the discharge of any type are the amount of energetic yield (quantity of NO or HNO_3 for 1 kWh of expended energy) and the concentration of the oxide obtained.

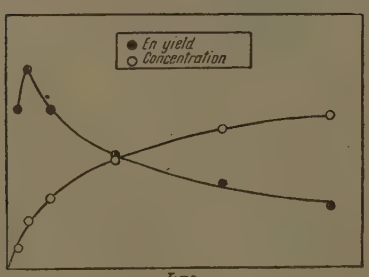

Fig. 3a.

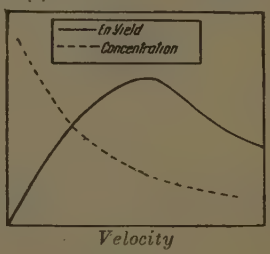

Fig. 3b.

As is known, the electric measurements at very high frequencies are very difficult and inaccurate. Therefore, in order to evaluate the power consumed in the torch we used the calorimetric method.

The outlines of this design are shown in Fig. 2: A—reaction vessel with a capacity of 3 l, K—glass calorimeter, M—motor with a mixer, T—Beckman thermometer, E—electrode, B—barometer; P—vacuum pump, C, C_2, C_3—washing phials, X_1, X_2—taps.

The water value of the calorimeter, determined by means of the nichrome heater fed with continuous current was 5561.3 cal. The small rise of temperature during the tests (0.4—0.8° C) and its short duration warranted such a small dispersion of the heat that it might be neglected.

The energy emitted in the calorimeter during a certain lapse of time was calculated after the formula $U = 0.06436 \cdot \triangle t$ kWh, where t is the increment of temperature.

The analysis of the products was performed after the method of evacuated vessel. The portion of the gas was sucked into a quite dry and evacuated vessel (0.5 l capacity). After this, water was introduced into the vessel. Sometimes hydrogen peroxide was added to the water to make oxidation of NO more complete.

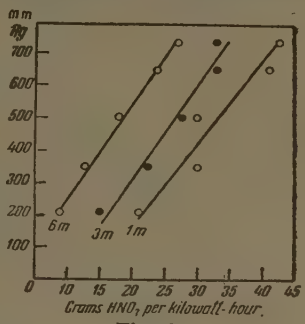

Fig. 4.

After the lapse of 30 min. during which the vessel was many times shaken, the contents of the vessel were transferred into a glass and titrated with caustic alkali.

From the results of the titration the absolute amount of the HNO_3 obtained, the energetic yield, and the concentration of NO formed in the discharge were calculated.

As the reduction of the nitric oxide takes place at the same time as it is formed, the energetic yield must depend on the time during which a given amount of gas will remain in the zone of discharge.

For the torch these data are represented in Table 1 and in Fig. 3

Table 1

Dependence of Yield and Concentration on Time

Duration of test in minutes	0.5	1	2	5	10	15
Energetic yield calculated in g HNO_3 for 1 kWh	36.6	45.6	36.6	24.7	19.5	14.2
Volume percentage of NO (approximate)	0.47	1.1	1.6	2.6	3.2	3.5

In comparing these results with the corresponding data for the arc[7] discharge (Fig. 4) it may be seen that the general aspect of dependence is similar in both cases, though, as regards the torch, the maximum on the curve is more sharply expressed.

The effect of pressure. During the formation of nitric oxide from O_2 and N_2 no change takes place in the number of molecules, therefore the change of pressure cannot alter the chemical equilibrium once established under given conditions. The factor of pressure can, however, influence the rate at which the equilibrium is obtained and it will therefore also influence the actual concentration of NO and the energetic yield of the same.

In contrast with other types of discharge the influence of pressure on the synthesis of NO in the torch is very considerable, as it will be seen from the description of the following experiments.

The experiments mentioned above were made at 5 different pressures below the atmosphere, the dependence of the energetic yield on time being determined for each pressure.

The conditions in all the cases observed were kept the same.

The results of the test are shown in Table 2 and in Fig. 4.

Table 2

Influence of Pressure on Energetic Yield and Concentration of NO

Pressure in mm Hg	1 min		2 min.		3 min.		6 min.	
	Energetic yield in g HNO_3 per 1 kWh	Vol. % NO	Energetic yield in g HNO_3 per 1 kWh	Vol. % NO	Energetic yield in g HNO_3 per 1 kWh	Vol. % NO	Energetic yield in g HNO_3 per 1 kWh	Vol. % NO
209.5	20.94	1.6	15.71	2.4	14.96	2.7	8.98	3.7
351.5	29.92	1.3	26.93	2.1	22.44	2.4	12.72	2.9
507.6	29.92	0.9	33.66	1.8	27.68	2.2	17.95	2.6
655.0	41.14	0.8	32.16	1.5	32.91	1.7	23.94	2.5
740.0	42.64	0.7	38.15	1.4	32.91	1.9	26.93	2.5

The linear dependence of yield on pressure observed within the whole range from 740 to 209.5 mm will be of considerable practical interest if it remains in the region of sufficiently great pressures. This problem is not solved as yet. Besides, both the regularity observed in the experiment and the change in the concentration of the NO obtained with pressure may in our opinion presumably contribute in explaining the chemical processes which take place in the torch discharge. N. I. Nekrasov[8] has shown that the formation of chemically active particles in electric discharges is connected with the process of recombination, the possibility of which increases with the decrease of the velocity of negative particles—ions and electrons. If we apply this conception to the torch discharge, the influence of pressure may be interpreted in the following way:

At high pressures of gas mixtures the lengths of free paths of molecules and ions are small. Between the collisions ions and electrons cannot noticeably increase their velocity, and stay slow.

This increases the probability of the recombination with positive ions.

On the other hand, the possibility of abstraction of the surplus energy by means of neutral molecules, playing the role of «third body», is also increased at high pressures.

The study is carried on further in the following directions:

1. NO synthesis at high pressures. 2. Kinetics of the process. 3. Influence of electrode material and of electric conditions in the torch.

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CHEMICAL PHYSICS

THE REGION OF THE TWO-STAGE SPONTANEOUS IGNITION OF HYDROCARBONS

By A. V. BELOV and M. B. NEUMANN

(Communicated by N. N. Semenov, Member of the Academy, 23. XII. 1937)

1. Introduction. As was shown by one of the authors of this paper (1) the spontaneous ignition of methane, ethane and pentane within the temperature range 500—800° C proceeds according to the theory of degenerate explosion developed by N. N. Semenov (2).

Under these conditions in the mixture of hydrocarbons and oxygen, an autocatalytic reaction takes place, the velocity of which changes according to the law

$$w = Ae^{\varphi t}. \qquad (1)$$

50% of hydrocarbon being oxidized, the velocity of the reaction begins to decrease.

If the initial pressure exceeds the critical value P_k, then, a certain time after the admission of the mixture in a heated vessel, the velocity of the reaction reaches such a value that the heat evolved can no longer escape through the walls of the wessel, the mixture begins to heat up and finally the process ends in a hot explosion.

The reduction of the induction period of spontaneous ignition under the increase of initial pressure and temperature can be calculated according to the formula

$$\tau p^n e^{-\frac{\gamma}{T}} = \text{const.} \qquad (2)$$

Within the temperature range 250—400° C the spontaneous ignition as has been shown by Aivazov and Neumann (3), occurs in another way.

In the oxygen or air mixtures of hydrocarbons, heated up to the above mentioned temperature there proceeds a relatively slow chain reaction, ending in the appearance of a cold flame, if the initial pressure exceeds the value p_1.

The induction period of a cold flame τ_1, decreases with the increase of pressure and temperature. If the initial pressure exceeds a certain value p_2, then within a short time τ_2 after the appearance of the cold flame, the explosion takes place.

We, thus, see that the spontaneous ignition of hydrocarbons in the temperature region 250—400°C has a two-stage character.

2. Results of the experiment. The present investigation was undertaken to prove the applicability of the theory of two-stage spon-

taneous ignition of hydrocarbons at pressures above the atmospheric pressure. The method used in this work consisted in the admission of a mixture of pentane and air in a hot steel bomb and in the photorecording of the curve of pressure change on a moving sensitive paper.

The moments of the admissions of the mixture, appearance of the cold flame and beginning of the explosion are clearly shown on the curves of pressure change obtained.

The experiments were carried out with air mixtures of pentane of various concentration. For each mixture the induction periods τ_1 and τ_2 of the hot and the cold flame were determined at different temperatures and pressures.

If the experiments are carried out at a constant temperature, then, with the increase of initial pressure p, the induction period of a cold flame is regularly reduced, as shown, for instance, in Table 1.

Table 1

Change of Induction Period of a Cold Flame of 3.1% Mixture of Pentane and Air Depending upon the Pressure at $T = 318$ °C

p kg/cm²	1.05	1.2	1.5	1.9	2.4	3.0	3.2	3.9	4.3
τ sec.	13.0	10.5	8.0	7.0	6.8	6.6	6.5	1.2	0.7

Under initial pressures, lying between 3.5 kg/cm² and 3.9 kg/cm² a cold flame is transformed into a hot one and a two-stage spontaneous explosion is thus observed.

Within this range of pressures the induction period of cold flame is steadily reduced.

With the increase of pressure above 3.9 kg/cm² a sharp decrease of the induction period of spontaneous ignition is observed, no traces of appearance of a cold flame being observed on the indicator diagram. The explosion occurs in one stage and judging from the curves of the increase of the pressure, the kinetics of the reaction, proceeding during the induction period, can be described by the law (1), following from the theory of the degenerate explosion.

Similar results were obtainend at various temperatures from 270 to 400°C with this mixture and also with air mixtures of pentane of different composition.

In Table 2 results of experiments with a 3.1% mixture of pentane at $T = 318$°C are given.

Table 2

Change of Induction Period of a Cold Flame of 3.9% Mixture of Pentane and Air Depending upon the Pressure at $T = 318$ °C ($p_1 = 1.25$ atm, $p_2 = 3.0$ atm, $p_3 = 3.5$ atm)

p kg/cm	1.27	1.45	1.65	2.1	2.5	2.95	3.1	3.5	3.7	3.85
τ sec	19.2	14.0	13.0	10.1	9.0	8.0	7.8	1.8	1.5	1.3

Thus it turns out that the region of a two-stage spontaneous ignition of pentane is limited not only with respect to temperature, but also to pressure. The results of our experiments with a 3.9% mixture are shown in the Figure.

The region of the cold flame is limited by small circles, the region of one-stage ignition by points.

The region of two-stage ignition is shaded.

A similar picture was observed with air mixtures of pentane of various concentrations and also with mixtures of diisopropyl ether and air.

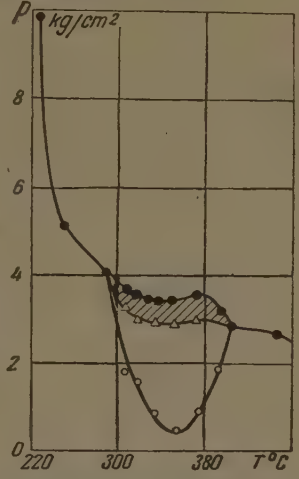
In all the cases investigated there existed, besides the critical pressure p_1 of the appearance of cold flame and the lower limit p_2, an upper limit p_3 of a two-stage spontaneous ignition.

This phenomenon of the upper limit of the pressure of two-stage spontaneous ignition is, apparently, widely spread and takes place in the hot inflammation of alyphatic hydrocarbons of various structure.

3. Discussion of results. The results obtained can be explained if we suppose that in the mixtures of hydrocarbons and air or oxygen two parallel oxidation reactions take place. The first of these reactions proceeds according to the mechanism of degenerate explosion, its velocity being expressed by formula (1).

The velocity w_1 of this reaction increases rapidly with the increase of pressure.

From our experiments on the change of induction period of spontaneous ignition at high pressures and temperatures it can be concluded that the parameter φ appearing in formula (1) increases as p^3 of p^4.



Regions of cold and hot flame in a 3.9% mixture of pentane with air.

The second reaction is connected with the accumulation, during the induction period, of peroxides, which disintegrate when their concentrations reach certain critical values.

This disintegration leads to a high concentration of radicals or other active centres, and, as a result, a cold flame appears. At sufficiently high pressures the cold flame is changed into a hot one. The mechanism of the second reaction, which leads to the appearance of a cold flame, has been experimentally proved by Neumann and Tutakin (4).

The velocity W_2 of this reaction increases with the pressure much more slowly than W_1. The velocity of the oxidation process at lower pressures in the first approximation is therefore equal to W_2 and the reaction leads to the formation of a cold flame.

At high pressures, when $W_1 \gg W_2$, the cold flame cannot form, because the rate of the first process is so rapidly accelerated that the self-heating begins a long time before the critical concentration of peroxides is attained, which leads to the appearance of the hot flame.

The observed phenomenon is of a great importance for the theory of detonation in petrol engines.

Some investigators connected this phenomenon with the appearance of a cold flame in the engine. However, the possibility of formation of a cold flame of hydrocarbons at high pressures, occurring in an engine at the end of combustion, is made rather doubtful by our experiments.

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PHYSIQUE DU GLOBE

DOSAGE DE L'OZONE ATMOSPHÉRIQUE À L'ALTITUDE DE 13 ET 14 km

Par M. KONSTANTINOVA-SCHLESINGER

(Présenté par S. I. Wawilow, de l'Académie, le 8. I. 1938).

C'est en juillet 1936 que pour la première fois la teneur en ozone de l'air pris par un substratostat à 10 km d'altitude environ a été évaluée par un procédé direct.

La méthode fluorométrique du dosage de l'ozone élaborée par l'auteur d'après les idées générales énoncées par S. Wawilow, de l'Académie, étant bien plus sensible que toute autre méthode chimique, c'est en l'appliquant que nous avons pu effectuer le dosage de l'ozone dans une quantité d'air aussi petite.

Récemment nous avons évalué par le même procédé la teneur en ozone de l'atmosphère à 13 et 14 km d'altitude. L'air a été pris au moyen de ballon système GECh par le lieutenant Romanow, chef de l'équipage, pilotant le substratostat, et par Chitow, membre de l'équipage, ingénieur du 3-me rang. Les résultats de la détermination de la concentration de l'ozone dans les trois ballons qui nous ont été envoyés sont exposés sur le tableau ci-dessous:

Tableau 1.

Altitude (mètres)	$t°$ C	Concentration de l'ozone		
		g/l	moyenne	cm/km
14 300—13 800	—56.2— —53	$1.06 \cdot 10^{-7}$	$9.97 \cdot 10^{-8}$	0.00466
14 100—13 500	—54.9— —51	$9.35 \cdot 10^{-8}$		
13 300—12 800	—49.7— —46.5		$9.76 \cdot 10^{-8}$	0.00455

Ainsi pour le moment nous disposons des dosages fluorométriques de la concentration de l'ozone à six altitudes différentes (tableau 2).

La courbe de distribution de l'ozone pour les 14 premiers kilomètres d'altitude, déduite de ces données, est montrée dans la fig. 1.

À titre de comparaison nous donnons dans la fig. 2 les courbes de distributions de l'ozone trouvées par différents auteurs au moyen de procédés optiques-indirects.

Les courbes *1* et *2* sont déduites par l'application du «Umkehreffekt» de Götz à l'étude des spectres du ciel bleu; la courbe *1* est celle de Götz, Meetham et Dobson à Arosa; la courbe a été trouvée par Dobson et Meetham dont les mesures ont été effectuées à Tromsö. La courbe *3* nous montre la distribution

Tableau 2

Concentration de l'ozone à différentes altitudes

Lieu	Altitude (kilomètres)	Concentration de l'ozone g/l · 10^{-8}	Concentration de l'ozone cm/km
Stratosphère	14	9.97	0.00466
	13	9.8	0.00455
	9.6	8.7	0.00404
Mont Elbrouz	4.3	7.3	0.00340
	2.2	5.7	0.00268
Moscou	0.1	<2.0	<0.00092

de l'ozone d'après Regener. La courbe *4*, ainsi que la courbe *3*, a été déduite des données sur la densité optique au-dessus du spectateur; quant aux densités optiques, O'Brien, l'auteur de cette courbe, les a trouvées par l'analyse des spectres de la lumière solaire, photographiés à différentes altitudes pendant l'ascension du Stratostat «Explorer II» en novembre

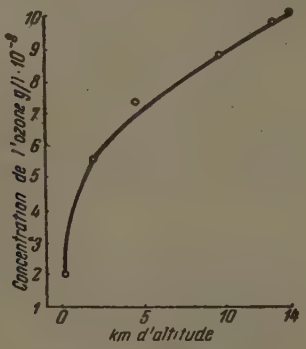

Fig. 1. Courbe de distribution de l'ozone

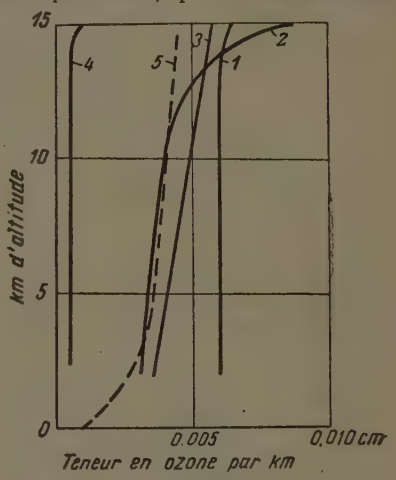

Fig. 2. Courbes de distribution de l'ozone.

1935. La courbe *5* c'est la nôtre, étant le résultat des mesures directes effectuées par la méthode fluorométrique. Malheureusement, nous ne disposons pas encore d'air pris à des altitudes plus grandes; notre courbe «fluorométrique» n'a donc pu être prolongée que jusqu'à 14 km, tandis que toutes les autres atteignent des altitudes au-dessus de 20 km.

Il est indispensable de prolonger le dosage direct de l'ozone à de plus grandes altitudes en effectuant en même temps des analyses fluorométriques de l'air pris à de petites altitudes. Ce n'est que par de pareilles analyses d'air, pris le même jour à différentes altitudes, qu'on pourrait être persuadé que les variations de la quantité absolue de l'ozone n'influent pas sur les résultats gagnés.

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CHEMISTRY

THE COMPOSITION OF SOME GOLD AND TUNGSTEN CYANIDES

By M. M. RAINES

(Communicated by V. E. Tiščenko, Member of the Academy, 25. XII. 1937)

It is known that on double decomposition of salts and acids in aqueous solutions, an equilibrium is established, after which the weak acid anion may be substituted by an equivalent amount of the strong acid anion.

This is true for the reactions in solutions which do not involve any secondary processes, namely formation of insoluble salts of the weak acid or formation of other—even soluble—complex compounds with weak acid anion.

In the course of investigation of the action of hydrocyanic acid on gold and tungsten chlorides we have had the opportunity to observe the influence of formation of complex compounds on the reactions of hydro-cyanic acid with metal chlorides.

I*. The action of hydrocyanic acid on gold chloride solution results in the formation of the gold-hydrocyanic acid $HAu(CN)_4 \cdot 3H_2O$ with evolution of hydrogen chloride:

$$HAuCl_4 + 4HCN \rightleftarrows HAu(CN)_4 + 4HCl.$$

Consulting literary data one sees that there is no agreement among the authors as to the formula of the tervalent gold cyanide. Some of them suppose it only as $Au(CN)_3 \cdot 3H_2O$(1), others suggest that its existence in the form of $HAu(CN)_4 \cdot 1\frac{1}{2}H_2O$(2) is also possible, others apply to this cyanide the doubled formula: $Au_2(CN)_6.6H_2O$. This uncertainty of composition resulted in inexact notions of structure and incorrect reasoning about the properties of this compound, in which the existence of a complex anion $[Au(CN)'_4]$(1) is persistently denied.

The analysis of the obtained cyanide is as follows:

$$Au = 51 \cdot 75\%;\ CN = 27 \cdot 39\%;\ H_2O = 15 \cdot 45\%.$$

The ratio $Au : CN : H_2O = 0.992 : 4 : 3$.

II**. The action of hydrocyanic acid on tungsten chloride results in the formation of a tungsten-cyanic acid solution which on neutralization gives a salt of the following composition $K_4[W(CN)_8].2H_2O$.

Thus, for instance, hydrocyanic acid, passed through a chlorotungstate solution $K_3W_2Cl_9$, displaces the hydrogen chloride from the latter:

$$K_3[W_2Cl_9]' + 16HCN \rightleftarrows 2\ [W(CN)_8]'''' + 6Cl' + 3KCl + 16H^{\cdot}.$$

* The study was carried out in 1934 by B. A. Caplan, A. R. Putning and M. M. Raines.

** The investigation was carried out by O. A. Žurid, M. M. Raines and Z. A. Timofeeva in 1936.

After neutralization of this solution with caustic potash and addition of alcohol a salt precipitates, the composition of which upon recrystallization from the diluted alcohol corresponds to the tungsten cyanic potassium formula $K_4W(CN)_8 \cdot 2H_2O$.

The same salt has been obtained by Olsson[4] and Collenberg[5] out of potassium chlorotungstate and potassium cyanide [see also Rosenheim and Deni[6]].

Conclusions

a) According to elementary analysis the composition of gold-hydrocyanic acid must be expressed by the formula

$$H[Au(CN)_4] \cdot 3H_2O;$$

its stability in solution is due to the formation of a stable complex compound $[Au(CN)_4]'$.

b) The crystal-optical investigations carried out by M. P. Golovkov have shown that isolated crystals of this acid have a particular structure of their own.

c) The two examples mentioned above show that, owing to formation of complex ions, the metal-cyanic acids and their salts can be obtained by direct action of hydrogen cyanide on metal chlorides.

Acknowledgements are due to the member of the Academy of Sciences V. E. Tiščenko by whose valuable advice and instructions we have profited in the course of these two investigations and of other works on the production of complex cyanide compounds.

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CHEMISTRY

HYDROXYLAMINE COMPOUNDS OF PALLADIUM. I

By V. I. GOREMYKIN

(Communicated by N. S. Kurnakov, Member of the Academy, 28. XII. 1937)

As early as in 1871 Losson(1) showed that hydroxylamine gives complex compounds with bivalent platinum. The hydroxylamine molecule occupies only one coordination place, most frequently displaying neither acid nor basic properties and according to I. I. Černiajev (2) brings about the bond, with the central atom through nitrogen.

The hydroxylamine compounds of platinum are relatively stable both in aqueous solution and in solid state, although in the course of time a marked decomposition takes place under the influence of the sun rays and especially heat; they should therefore be kept in a dark place. The reducing reaction is very rarely observed under usual conditions, unless the complex contains an acid residue of a reducing nature, e. g. NO_2. Recent research in this field carried out by L. A. Chugaeva and I. I. Černiajev(3), I. I. Černiajev (4), I. I. Černiajev and V. I. Goremykin (5) has proved that one is able to realize the synthesis of complex compounds of platinum containing hydroxylamin in different combinations with other amines—ammonia, pyridine. It has been experimentally established that the stability of the bond of pyridine, ammonia and hydroxylamine with the central atom of platinum in acid and neutral solutions gradually decreases in the direction from pyridine to hydroxylamine and is but little influenced by the composition and structure of the whole complex. In alkaline solutions pyridine is splitting off sooner than other amines, but the reducing reaction occurs neither in acid nor in alkaline solutions.

Examining the literary data we did not succeed in establishing the existence of complex compounds containing both hydroxylamine (or hydroxylamine in different combinations with other amines) and palladium. Therefore we set ourself the task to make up this deficiency by 1) synthesizing the hydroxylamine compounds of palladium, 2) studying their properties, structure, transformations, reactions of exchange, and 3) establishing whether isomerism will be observed in these compounds. If we were successful in obtaining but two types of hydroxylamine compounds of palladium, e. g. tetramines and diamines, we could proceed to the problem of the influence of the nature of the central atom of the complex on the stability of hydroxylamine compounds. In this investigation we hoped to discover both the analogies and differences between the hydroxylamine compounds of palladium and platinum. There were some grounds to expect a successful solution of this problem, since these elements are analogous in many their properties, in the

type of chemical compounds they form and up to their place in Mendeleev's table.

The experiments on the production of hydroxylamine compounds of palladium carried out by the author supported his assumption. The author succeeded in separating several hydroxylamine compounds of palladium in a pure state, their composition being of the following types: $|Pd4A|x_2$; $|Pd2Ax_2|$; $|Pd4A||Ptx_4|$; $|Pd2A_12\ A_2||Ptx_4|$.

Tetrahydroxylamine-dihydroxo-palladium $|Pd4Hx|(OH)_2$*. The base $|Pd4Hx|(OH)_2$ is formed on interaction of potassium chloropalladite with an excess of hydroxylamine hydrochlorate in the presence of an equivalent quantity of 1% sodium hydroxide. The reaction proceeds in strongly diluted solutions in the cold, according to the equation:

$$K_2|PdCl_4| + 4Hx \cdot HCl + 6NaOH \rightarrow |Pd4Hx|(OH)_2 + 2KCl + 4H_2O.$$

Tetrahydroxylamine-dihydroxo-palladium is a colorless crystalline substance, insoluble in cold water, alcohol or ether. Under usual conditions rather stable. In the light a marked decomposition takes place. When heated it is almost instantaneously reduced to metal. The base $|Pd4Hx|(OH)_2$ carefully washed with water and strong alcohol can be preserved for weeks in a dark place. This compound resembles very much Alexander's base $|Pt4Hx|(OH)_2$ in the way in which it is obtained, in its composition and low solubility, but it is distinguished from the same by it being easily reduced to metal when heated or placed in an alkaline solution.

Salts of the Base $|Pd4Hx|(OH)_2$. The base $|Pd4Hx|(OH)_2$ is readily soluble in diluted acetic and sulphuric acids in the cold, but the salts of these acids have been not as yet separated in a pure state by the author. This may be put down to they being very easily soluble in water. In aqueous solution these salts are rapidly hydrolized with separation of palladium.

The action of oxalic acid upon solutions of these salts produces an abundant precipitate of a colorless crystalline substance, showing under the microscope long needles of $|Pd4Hx|C_2O_4$. The oxalate is hardly soluble in cold water and alcohol; it is not stable. In the course of time the colorless long needles become first grey and then black, this being probably an evidence of the decomposition of the complex. Contrary to palladium oxalate the platinum tetramine oxalate $|Pt4Hx|C_2O_4$ specially synthesized and tried by the author is distinguished by its stability both in aqueous solution and in solid state.

The solution of acetate of base $|Pd4Hx|(OH)_2$ is used for the production of chloroplatinite $|Pd4Hx||PtCl_4|$. If a solution of potassium chloroplatinite comes into contact with the acetate of base $|Pd4Hx|(OH)_2$, there is immediately produced chloroplatinite $|Pd4Hx||PtCl_4|$ in the form of pinkish long needles hardly soluble in cold water and alcohol.

Chloroplatinite $|Pd4Hx||PtCl_4|$ is rather stable and remains almost unchanged with time. When recrystallized it disintegrates. The complex compound obtained and tried by the author, chloropalladite $|Pt4Hx||PdCl_4|$ is an isomer of chloroplatinite $|Pd4Hx||PtCl_4|$ and is distinguished from the latter by a higher stability, and pronounced crystallization: long, thick, green-colored needles; under usual conditions no signs of decomposition of the complex are observed.

Trans-Dihydroxylamine-dichloro-palladium $|Pd\ 2Hx\ Cl_2|$. This non-electrolyte may be readily obtained in the cold by the action of diluted hydrochloric acid upon the base $|Pd4Hx||(OH)_2$

* NH_2OH, Hx denotes hydroxylamine.

or on the acetates, sulphates, and oxalates of this base, according to the equation:

$$|Pd4Hx|(OH)_2 + 4HCl \rightarrow |Pd2HxCl_2| + 2H_2O + 2HxHCl.$$

The easy splitting of the tetramine $|Pd4Hx|x_2$ by slightly diluted hydrochloric acid under normal conditions may be explained by the unstable bond between hydroxylamine and palladium, since as to the method of its production, its composition and other properties, $|Pd2HxCl_2|$ closely approaches to the non-electrolyte of Alexander, $|Pt2HxCl_2|$. Taking into account that the disintegration reaction (judging by the chemical products) follows the rule of Jörgenssen, the author ascribes the trans-form, $|Pd2HxCl_2|$, to this complex compound. Certainly, a more close study of the non-electrolyte $|Pd2HxCl_2|$ will enable the author to supply additional data concerning the structure of this compound.

Trans-$|Pd2HxCl_2|$ is a yellow crystalline substance (long, thick needles), readily soluble in water, less so in diluted strong alcohol. In an aqueous solution becomes immediately hydrolized, therefore it is impossible to determine its electric conductivity.

Trans-$|Pd2HxCl_2|$ is dissolved in diluted ammonia with formation of the tetramine $|Pd2Hx2NH_3|\ Cl_2$; the attempts of separating the latter in a pure state have been as yet unsuccessful.

A solution of the tetramine $|Pd2Hx2NH_3|\ Cl_2$ slightly acidulated with acetic acid produces an abundant precipitation of chloroplatinite, $|Pd2Hx\ 2NH_3|\ |PtCl_4|$ when treated with potassium chloroplatinite.

Chloroplatinite $|Pd2Hx2NH_3|\ |PtCl_4|$ presents long needles of a pinkish color, hardly soluble in water and alcohol. The analytical data obtained are in perfect agreement with the formula ascribed to it. The investigation is being continued.

Conclusions

1. Hydroxylamine is able to penetrate into the complex molecule $K_2|PdCl_4|$ in a neutral and slightly alkaline solution, and forms the base $|Pd4Hx|(OH)_2$.

2. Comparative data show that hydroxylamine compounds of palladium are less stable than the hydroxylamine compounds of platinum of the same type.

3. The bond hydroxylamine—platinum is stronger than the bond hydroxylamine—palladium in compounds of the same type.

4. Hydroxylamine compounds of palladium of the Magnus salt type $|Pd4A|\ |Ptx_4|$ are very stable and in this respect resemble the complexes of platinum.

5. The following hydroxylamine complex compounds of palladium and platinum have been obtained and studied for the first time: $|Pd4Hx|\ |(OH)_2$; $Pd4Hx|C_2O_4$; Trans-$|Pd2HxCl_2|$; $|Pd4Hx|\ |PtCl_4|$; $|Pd2Hx2NH_3|\ |PtCl_4|$; $Pt4Hx|C_2O_4$; $|Pt4Hx|\ |PdCl_4|$.

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CHEMIE

PHYSIKALISCH-CHEMISCHE FORSCHUNGEN IM PRIMORSKIJ RAYON DER KALMÜCKISCHEN ASSR IM JAHRE 1937

V. I. NIKOLAJEV, O. K. JANATJEVA und M. A. FRISCHMUT

(Vorgelegt von N. S. Kurnakov, Mitglied der Akademie, am 28. XII. 1930)

In der vorliegenden Arbeit werden kurz die Resultate der Expeditionsforschungen und die im Laboratorium erzielten Ergebnisse der Bearbeitung des Expeditionsmaterials aus dem Primorskij Rayon der Kalmückischen ASSR dargelegt.

Die chemische Zusammensetzung der Tiefenwässer aus Bohrlöchern bis zu 200 m Tiefe wird durch folgende Besonderheiten charakterisiert (s. die ersten 9 Zeilen der Tabelle).

Der Kaliumionengehalt in der Salzzusammensetzung der Wässer betrug mehr als 0.56%, d. h. er war grösser als das Kaliumionengehalt im Wasser des Kaspischen Meeres (1). Besonders gross ist die Kaliumionenkonzentration für das Wasser aus dem Bohrloch No 1 im Gebiet des Sowkhos Ulan-Tug, nämlich: 3.38% $K^{\cdot}$(6.44% KCl), für das Wasser aus dem Bohrloch No 2 des Sowchos Ulan-Khejtsch 1.73 $K^{\cdot}$(3.30% KCl) und für das Wasser des Bohrlochs No 4 1.51% $K^{\cdot}$(2.88% KCl).

Es ist ratsam, das Verhältnis der Kaliumionengewichtsprozente zu den Natriumchloridgewichtsprozenten im trockenen Rückstand d. h. die Grösse $\frac{K^{\cdot}}{NaCl}$, als Kontrollkoeffizienten zu benutzen.

Nach den Angaben von Lebedinzew ist dieser Wert für das Kaspische Meerwasser sehr klein, nämlich 0.009.

Fast für alle Tiefenwässer ist der Kontrollkoeffizient bedeutend grösser als 0.009, wobei er für das Wasser aus dem Bohrloch No 1 des Sowchos Ulan-Tug den Wert 0.134 erreicht, der 16 mal so gross als der für die Salzzusammenzetzung des Kaspischen Meeres ist.

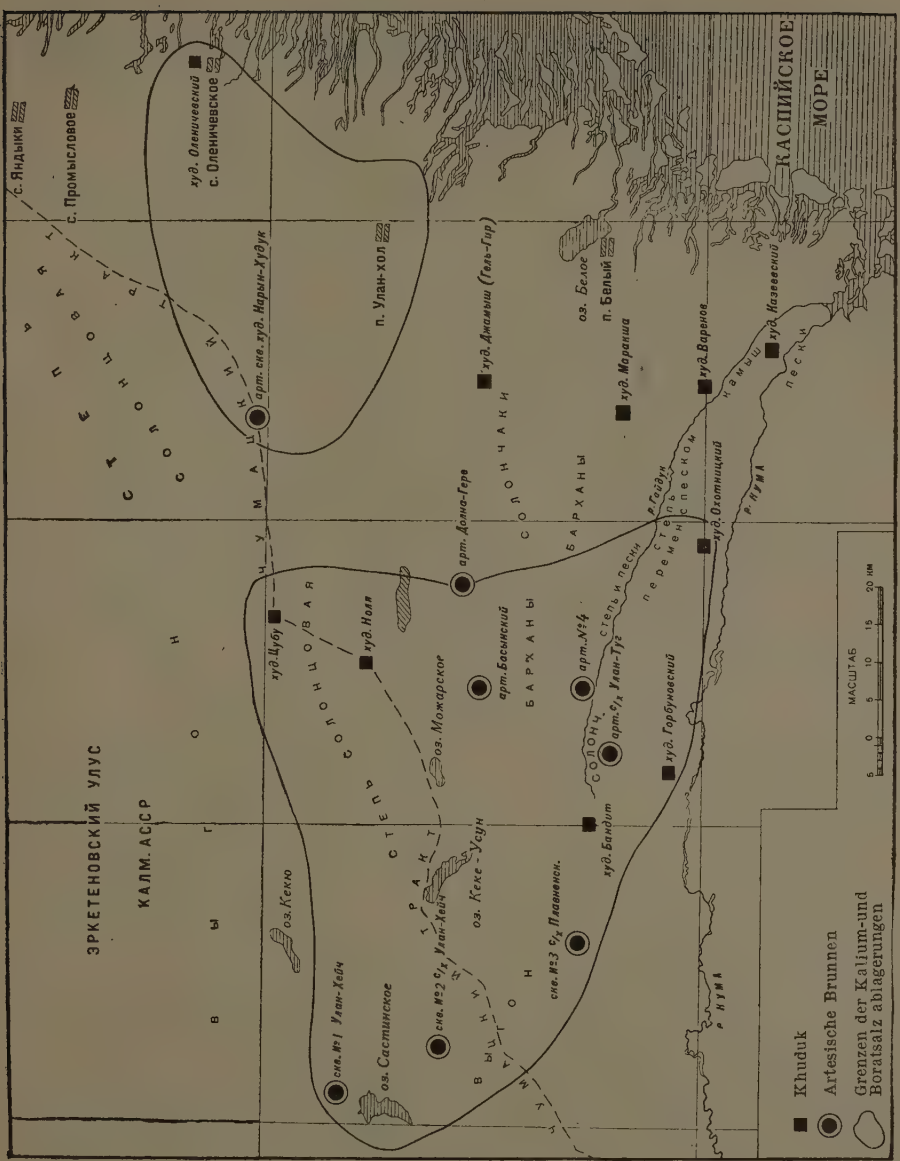
Ebenso übertrifft der Bromionengegalt im Salzbestand der Wässer 0.06% Br'—eine Grösse, die für das Kaspische Meer charakteristisch ist und für die obengenannten Bohrlöcher 0.46 (!), 0.34 und 0.24% Br' erreicht.

Besonders interessant sind die Hinweise auf einen ungewönlich hohen B_2O_3-Gehalt im Salzbestand nicht nur der artesischen Tiefenwässer sondern auch der Khuduken (von im ganzen 4—6 m Tiefe). Die Gewichtsprozente von B_2O_3 erreichen in vielen Fällen bis 0.7; 0.8 und 0.9% B_2O_3 von dem Salzbestand des Wassers.

Sogar das Wasser eines kleinen, flachen Flüsschens in der Nähe der Siedlung Ulan-Khol (s. die halbschematische Karte) enthält 0.94% B_2O_3 und 1.33% $K^{\cdot}$ (2.59% KCl) im Salzbestand.

Hiervon sprechen auch die Khudukenwässer aus verschiedenen Stellen des Primorskyij Rayon, wenn auch in weniger klarer Form.

Bezeichnung des artesischen Brunnens oder Khuduks	Gewichtsprozent d. trockenen Rückstands			Salzbestand des Wassers in Gewichtsprozenten														
	K^+	Br^-	B_2O_3	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$Fe(HCO_3)_2$	$NaHCO_3$	$CaSO_4$	$MgSO_4$	$MgCl_2$	KBr	$MgBr_2$	KCl	NaCl	Na_2SO_4	B_2O_3	Salz-Summe	Trockener Rückstand
Naryn-Khuduk, art. Bohrloch № 1	0.97	0.24	0.57	0.0387	0.0656	0.0223	0.0776	0.0029	0	0	0.0043	0	0.0193	0.9492	0	0.0068	1.1867	0.1867
Sowkhos Ulan-Khejtsch Bohrloch № 1	0.64	0.32	0.81	0	0.0018	0.0488	0.1724	0.0032	—	—	0.0015	—	0.0029	0.0752	—	0.0025	0.3082	0.3090
Sowkhos Ulan-Khejtsch Bohrloch № 2	1.73	0.24	0.82	0	0.0286	0.0487	0.1227	0.0037	—	—	0.0019	—	0.0170	0.3198	—	0.0045	0.5469	0.5480
Sowkhos Plawnenskij Bohrloch № 3	0.47	0.31	0.94	0.0073	0.0090	—	0.0798	—	—	—	—	0.0005	0.0011	0.0289	0.0007	0.0012	0.128	0.120
Sowkhos Ulan-Tug Bohrloch № 2	3.38	0.46	0.76	0	0.0066	0.0178	0.0873	0.0027	—	—	0.0012	—	0.0103	0.0430	—	0.0013	0.1702	0.1712
Bohrloch № 4	1.51	0.34	0.66	0.0308	0.0683	0.0398	0.0153	0.0039	—	—	0.0052	—	0.0261	0.8213	—	0.0068	1.0175	—
Artesischer Brunnen Basynskij	0.71	0.071	0.71	0.0182	0.0451	0.0089	0.111	—	—	—	0.0007	—	0.0087	0.521	Freie H_2S=0.0085(Geruch) 0.0046	0.0048	0.679	0.672
Artesischer Brunnen Dalna-Gere	0.54	0.169	0.32	0.038	0.0716	0.0070	0.097	—	—	—	0.0028	—	0.0095	0.812	0.072	0.0035	1.113	1.00
Flüsschen Ulan-Khol 33 km nach Süden v. D. Olenitschewo nebst d. D. Ulan-Khol	1.33	0.11	0.94	0.0294	—	—	—	0.0165	0.0520	0.0030	—	0.0003	0.0049	0.0735	—	0.0017	0.181	0.172
Naryn-Khuduk Khuduk	0.417	0.139	0.591	0.049	0	0	0	0.024	0.001	0.034	0	0.0005	0.0025	0.168	0	0.0030	0.282	0.288
Nolia-Khuduk	0.116	0.127	0.73	0.0207	0.0425	0	0.0684	0	0	0	0.0018	0	0.0009	0.791	0.0217	0.0069	0.953	0.946
Zubu-Khuduk	0.378	0.043	0.163	0.0842	0	0	0	0.0425	0	0.2477 $+CaCl_2$= =0.0213	0	0.0010	0.0150	1.7556	0	0.0034	2.095	2.091
Bandit-Khuduk	0.21	0.04	0.46	0.0849	0.0361	—	—	—	0.1386	—	—	0.0002	0.0025	0.1777	0.1055	0.0025	0.5480	—
Gorbunowskij-Khuduk	0.95	0.036	0.049	0.050	—	0.010	—	0.042	0.268	0.012	0.0006	—	0.0181	0.615	—	0.0005	1.017	1.021
Okhotnizkij-Khuduk	0.82	0.051	0.066	0.064	—	0.0089	—	0.074	0.111	—	0.0004	—	0.0078	0.0125	0.1189	0.0004	0.512	—
Barenova-Khuduk	0.151	0.008	0.034	0.041	—	—	—	0.224	0.218	0.365 $+CaCl_2$= =0.358	0.0006	—	0.014	3.768	—	0.0017	4.991	5.050
Kiseewskij-Khuduk	0.21	0.03	0.21	0.0677	—	—	—	0.1590	0.2121	0.1142	—	0.0005	0.0049	0.6095	—	0.0027	1.173	0.180
Djamysch-Khuduk	0.21	0.15	0.15	0.0717	—	—	—	0.0609	$CaCl_2$= =0.0620	0.1245	—	0.0818	0.0047	0.7450	—	0.0016	1.0722	1.110
Marakscha-Khuduk	0.16	0.08	0.17	0.0560	—	—	—	0.1409	0.1336	—	—	0.0009	0.0028	0.4661	0.1412	0.0016	0.9431	0.926
Olenitschewo-Khuduk	2.36	0.07	0.87	0.0526	0.0172	—	—	—	0.0158	—	—	0.0001	0.0062	0.0430	0.0021	0.0011	0.126	0.121



So beträgt für den artesischen Brunnen im Rayon Naryn-Khuduk der Gehalt an B_2O_3 im trockenen Rückstand 0.57% und für den Khuduk—0.59%, der Gehalt an Bromionen für den artesischen Brunnen—0.24%, für den Khuduk—0.14%; die entsprechenden Werte des Kaliumionengehalts sind 0.97, und 0.42%. Der Kontrollkoeffizient $\frac{K^{\cdot}}{NaCl}$ beträgt für den Khuduk 0.007, d. h. er ist gleich dem Kaspischen.

Wenn wir die Punkte mit klar ausgeprägten Hinweisen auf einen vergrösserten Gehalt an Kalium- und Bromionen, sowie an B_2O_3 in den Wässern auf eine Karte auftragen, so finden wir 2 Gebiete des Primorskij Rayons, wo das Vorhandensein der Tiefenablagerungen von Kali und Boraten zu vermuten ist.

Auf der beigelegten Karte sind diese 2 Gebiete durch geschlossene Kurven abgegrenzt.

Es ist auch anzunehmen, dass der Rayon des Sowchos Ulan-Tug und weiter nach Nordwesten zu, sowie der Rayon zwischen Olenitschew und dem Flüsschen Ulan-Khol für die Entdeckung von Kali- und Boratlagern am günstigsten erscheinen.

Die Frage, wieso sich in den Wässern der artesischen Bohrlöcher und Brunnen so beträchtliche Mengen an Borsäure angesammelt haben, kann man vorläufig mit der Vermutung beantworten, dass in den Tiefen eine Auswaschung der Boratablegerungen durch Wässer stattfindet, die mit Magnesiumsulfat angereichert sind.

Alle Seen des Primorskij Rayons werden gerade durch einen hohen $MgSO_4$- Gehalt in den Solen charakterisiert.

Nach einer liebenswürdigen Privatmitteilung von I. B. Feigelson (Saratow), wurde bereit von ihm das Gleichgewichtsdiagramm erhalten, das von einer Erhöhung der Löslichkeit des Borax unter dem Einfluss von Schwefelmagnesiumsalz zeugt.

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MINERALOGY

TERRIGENOUS MINERALOGICAL CASSITERITE-BEARING PROVINCES IN TRANSBAIKALIA

By S. G. SARKISIAN

(Communicated by F. Loewinson-Lessing, Member of the Academy, 1. I. 1938)

No light has been thrown up to now in the USSR upon the problems of paragenesis in placer deposits of useful minerals, particularly, cassiterite. Yet a corresponding study would have been of great theoretical and practical importance, since the character of the minerals found in the placer deposit would give us available indications in our prospecting researches.

From a detailed mineralogical and petrographical investigation of a friable cassiterite-bearing rock, and of some country rocks, made by the author in East Transbaikalia, a number of terrigenous mineralogical cassiterite-bearing provinces have been established, viz.:

scheelite-titanite province,
topaz-tourmaline »
gold-cassiterite »

These terrigenous mineralogical provinces are connected with the supplying provinces, the latter being chiefly composed of rocks of the granite family, enclosing quartz, quartz-feldspar, pegmatite and other veins containing cassiterite.

In the Imalkinsky deposit various granites and gneisses are developed, occurring in areno-schist sediments possibly of Triassic age. Cassiterite of a brown, yellow and, occasionally, black color occurs in quartz, quartz-feldspar and pegmatite veins, transecting both granites and areno-schist beds. Beside cassiterite, scheelite, wolframite and beryl are also encountered in these veins.

The whole of this complex of minerals of the supplying province, undergoing desintegration, is transported under the action of gravity and temporary streams, and produces eluvial and eluvial-deluvial placers of cassiterite. The smooth relief enables the friable material to be deposited near the supplying province, therefore the terrigenous mineralogical province fully reflects the character of the mineralogical composition of the supplying province. Scheelite and titanite are widely spread in friable deposits. The former originates from the same veins as cassiterite; the latter, from granites and gneisses. These two minerals as being the most resistant to weathering and accompanying cassiterite, characterize the Imalkinsky deposit. Apart from these minerals the following species have been reported from the Imalkinsky placer: quartz, feldspars, microcline, plagioclase, biotite, hornblende, almandite, hematite, magnetite, pyrrhotite, zircon, muscovite, augite,

andalusite, sillimanite, disthene, rutile, tourmaline, epidote, zoisite, tremolite, chlorite, gold (very rarely), monazite, wolframite and cassiterite.

Apart from the Imalkinsky deposit, the Zuk-Undur, Zavitinsky and Konginsky deposits are also referred to the scheelite-titanite and the cassiterite provinces. As regards the nature of the mineralization in situ the Sherlovaya Gora deposit presents a striking difference. A. K. Boldyrev and J. A. Louis think that «the cassiterite of the placer deposits originates from the same aquamarinetopaz rock crystal and greisen veins and stocks of the Sherlovaya Gora granite massif from which ferberite and basobismuthite have doubtlessly been brought.» Indeed, in the placers of Sherlovaya Gora, which may be, by the way, referred to the eluial-deluvial and the deluvial-alluvial type, both topaz originating from the above veins, and tourmaline originating from tourmalinized and ferruginated tufaceous quartz porphyres are widely spread.

The topaz-tourmaline association accompanying cassiterite enables the Sherlovaya Gora placers to be referred to the topaz-tourmaline terrigenous

mineralogical province. The grains of cassiterite are angular, irregular, occasionally prismatic with pyramidal terminations; the color is brown, dark-brown, black, occasionally with a reddish tinge. Some grains of cassiterite possess electromagnetic properties.

The third gold-cassiterite province comprising the Shilka-river basin from the village Borshchevka to the village Lomy, is sufficiently clearly distinguished from the two former terrigenous mineralogical provinces*.

Cassiterite is always attended by gold, and is encountered in flows in the graded alluvium. The grains of cassiterite are small, rounded and do not form large accumulations, since they are lost in the enormous mass of the alluvium. The colour of cassiterite varies within a wide range, from colourless to black.

The supplying provinces are the Sretensk-Nerchinsk and partially the Borshchevochny ranges.

In the summer of 1937 the author's party has discovered cassiterite in situ in the Farkovsky range (in pegmatite veins), in the valley of Dobrynin (the village Molodovsky in quartz veins), in the Akraisk columns (in pegmatite veins). Country gold deposits may formerly have existed and may still exist in these ranges; undergoing disintegration these deposits produced, together

* The alluvial sediments of the Shilka river downstream of the village Lomy have not been explored by the author.

with cassiterite-bearing veins, a deposit containing both gold and cassiterite. To the gold-cassiterite terrigenous mineralogical provinces the following deposits on the Shilka river may be referred: Farkovo, Ust-Kurlych, and a number of cassiterite and gold placers near the village Kalinovka in the vicinity of the station Kuenga, etc.

It should be noticed that the former two terrigenous mineralogical provinces are richer in cassiterite than the third one, since in this case cassiterite has not been subjected to distant transplacement, thus it had no time to mix up with sediments containing no cassiterite and to be deconcentrated, which is usually due to its low specific gravity.

Further mineralogical studies of the placer deposits of cassiterite should necesserily accomplish this scheme and extend the limits of these terrigenous mineralogical cassiterite provinces, establishing the connection which exists between them and the supplying provinces. Of no less importance is an experimental study of the changes in physical and chemical properties and of the stability of cassiterite varieties when transported in an aqueous medium. This is of high importance for the knowledge of the mechanism of accumulation and distribution of cassiterite in placer deposits, the more so that the stability of cassiterite during transportation has been insufficiently discussed in the works of Freise and Minler.

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MICROBIOLOGY

FORMATION OF GROWTH SUBSTANCES (AUXIN TYPE) BY BACTERIA

By E. A. RASNIZINA

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Owing to the recent advances in investigation of the rôle of growth substances in plant development, we can review from a new point the interrelation between higher plants and microorganisms and between the microorganisms themselves.

The power of bacteria to secrete growth substances allows us to explain the mechanism of the formation of tubercles on the roots of leguminous plants (1), tumours due to *B. tumefaciens* (2,3) and excrescences due to some fungi (4).

The rôle of the bacterial growth substances is not limited by the above examples. It is more than probable, that growth and development of plants are influenced by the bacterial growth substances, for some of the rhizosphera bacteria are mighty accumulated on the roots of plants and are permanently secreting growth substances.

Some data allow us to attribute an important rôle to the growth substances in the action of bacterial fertilizers on seeds. The study of the power of soil bacteria to produce growth substances is of great interest if one aims at approaching these complicated microbiological problems.

There are only few data on the production of growth substances (auxin type *) by bacteria. Boysen-Jensen (6) has shown that of 13 investigated species of bacteria the following 11 produce growth substances: 1) *Bact. xylinum*, 2) *Bact. radiobacter*, 3) *Bact. denitrificans*, 4) *Bact. coelicolor*, 5) *Bact. coli*, 6) *Bacill. mycoides*, 7) *Bacill. subtilis*, 8) *Bacill. vulgatus*, 9) *Proteus vulgaris*, 10) *Mycobacterium lacticola*, 11) *Mycobacterium album*.

The two species: *Bact. faecalis alcaligenes* and *Mycobacterium rubrum* do not produce growth substances at all.

In our research we were endeavouring to answer the following problems:

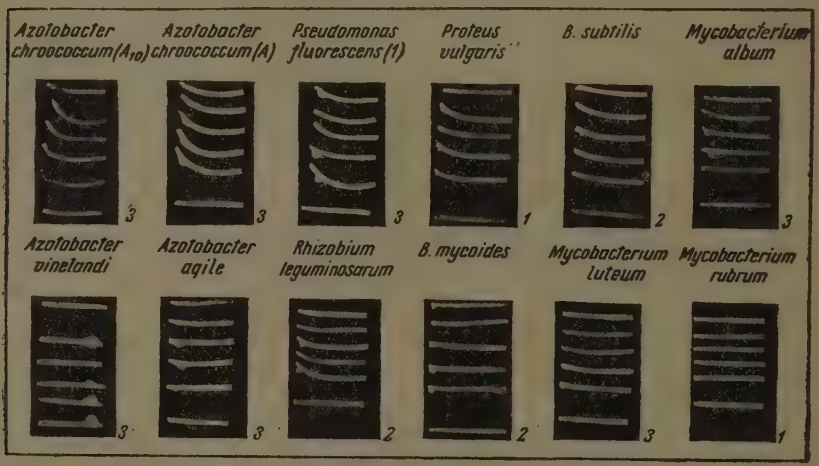
1. What are the differences between various species of bacteria in their power of producing growth substances?
2. Does this capacity depend on the genetic affinity of the bacteria?
3. How does this capacity change within the age of the culture?

The method of Boysen-Jensen was made use of; some modifications introduced by us are mentioned below. The bacteria were cultivated on meat infusion agar. A special kind of peptone was used, containing no growth

* Kögl (5) divides the growth substances in two types: 1) auxin type and 2) bios type. The auxin type includes auxin *a*, auxin *b* and heteroauxin.

substances of the auxin type. Azotobacter was cultivated on Ashby-agar. Each culture was tested after 2, 8, 16 and 24 days. The test was made in a different way than that of Boysen-Jensen. Instead of agar blocks we put a small quantity of bacterial slime on isolated and decapitated oat coleoptiles; the oats having been reared in the dark. The coleoptiles treated with the bacterial slime were placed in a dark moist camera at 22—23°.

4 hours after the degree of curvature was measured. The measurement was made on photoprints (Figure). First we used oat A—315, but afterwards



we gave preference to the variety «Pobeda»; the coleoptiles of the latter being more sensitive to the auxin action.

The results obtained are shown in the table.

Intensity of Growth Substances (Auxin Type) Produced by Different Bacteria

Bacteria	2 days	8 days	16 days	24 day
Azotobacter agile	6.0	3.6	2.4	8.2
» *vinelandii*	0.0	0.0	0.0	4.2
» *chroococcum* (str. A)	18.2	26.8	19.8	25.8
» » (str. 10A)	12.4	28.2	15.6	17.6
Bacterium coli	11.0	0.0	11.6	8.2
» *vulgare*	14.5	15.4	21.4	20.6
Bacillus mycoides (str. 3)	0.0	0.0	6.4	5.2
» » (II)	0.6	2.6	4.0	(15.6)
» » (л)	0.6	2.4	2.0	(10.6)
» » (21)	0.4	4.8	2.4	(11.8)
» *subtilis*	13.2	14.8	19.4	6.6
Mycobacterium album	11.0	14.4	29.8	25.0
» *luteum*	0.0	7.4	14.2	9.8
» *rubrum*	0.0	0.0	0.0	0.0
Pseudomonas fluorescens (str. 1)	10.4	21.4	17.0	11.6
» » (F-24)	11.0	8.8	8.8	5.2
» » (F-8)	26.6	8.6	6.6	17.4
Rhizobium leguminosarum (str. 1)	1.0	1.8	11.4	0.4
» » (2)	1.8	5.6	1.2	0.0
» » (3)	—1.0	8.0	3.0	—0.4
Sarcina lutea	12.0	10.0	22.6	10.2

1. As seen from the table, the soil bacteria possess a very different power in producing growth substances (Figure). We can divide the bacteria into three groups:

a) Bacteria which do not produce growth substances at all, or produce them in very small quantities. Those are: *Mycobact. rubrum* (0.0*), *Azotobacter vinelandii* (4.2), *Bacill. mycoides* (6.4), *Rhizobium leguminosarum* (strain 2) (5.6).

b) Bacteria which produce auxin with medium intensity. Those are: *Azotobacter agile* (8.2), *Rhizobium leguminosarum* (strain 1) (11.4), *Bact. coli* (11.6), *Mycobact. luteum* (14.2), *Pseudomonas fluorescens* (strain F-24) (11.0), *Bact. subtilis* (19.4).

c) Bacteria which produce the auxin with high intensity and in large quantities. Those are: *Bacterium vulgare* (21.4), *Pseudomonas fluorescens* (strain 1) (21.4), *Sarcina lutea* (22.6), *Pseudomonas fluorescens* (strain F-8) (26.6), *Azotobacter chroococcum* (strain A)(26.8), *Azotobacter chroococcum* (10A) (28.2), *Mycobacterium album* (29.8).

2. The power of auxin production does not depend on the genetic affinity of the bacteria. As seen from the data obtained, closely related species of the genus may strikingly differ as to their power to secrete growth substances of the auxin type:

Bacteria which produce no auxin at all, or produce them in small quantities:	Bacteria which produce the auxins with high intensity:
Bacillus mycoides, *Azotobacter vinelandii*, *Mycobacterium rubrum*.	*Bacillus subtilis*, *Azotobacter chroococcum*, *Mycobacterium album*.

3. Even various strains of the same species of bacteria differ in the intensity of auxin production. For instance, *Pseudomonas fluorescens*, *Rhizobium leguminosarum*.

4. The maximum of growth substances production is mostly observed in 8- and 16-day cultures. It does not coincide with the stage of active growth and multiplication of cells. Therefore one may suppose that the production of growth substances (heteroauxin) is connected with the dissimilative processes.

Thus, *Azotobacter chroococcum* and some strains of *Pseudomonas fluorescens* are the most intensive producers of growth substances among the rhizosphera bacteria. They may therefore be believed able to essentially influence the development of plants on whose roots they multiply.

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* The figures denote the maximum curvatures.

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MICROBIOLOGY

ON THE NATURE OF «AZOTOGENE» ACTION

By E. F. BEREZOVA, A. N. NAUMOVA and E. A. RASNIZINA

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«Azotogene» or «azotobacterin» is a bacterial fertilizing preparation, made from unsterilized peat by adding a suspension of a pure culture of *Azotobacter chroococcum*. It is introduced into the soil together with the seeds in the form of peat powder. As it has been established by Sheloumova ([1–3]) and Savostin ([4,5]) azotogene increases the yield of cereals and vegetables. The same results have been obtained in the practice of some experimental stations.

The positive results obtained by treatment with azotogene, have caused a production and probation of azotogene on a large scale. In this connection some uncertainties and difficulties have arisen which lead to the problem of the nature of azotogene action.

It was deemed up to now that azotogene action is due to the nitrogen fixation capacity of *Azotobacter chroococcum*. Azotobacter increases the nitrogen content of the soil and thereby increases the yield. We think this explanation fits, but exact prooves are wanting; especially in the cases when azotogene produces a positive effect on soils provided with nitrogen.

Without dwelling upon the analysis of this current explanation (and some other variants of it) we will direct our attention to a completely different mecanism of azotogene action, namely, the stimulating action which *Azotobacter chroococcum* produces on plants by means of secreting growth substances (auxin type).

The conception we developed here is based on numerous experiments carried out during the last two years. As far as azotogene is concerned, the main conclusions of our investigations run as follows:

1. *Azotobacter chroococcum* belongs to soil bacteria, which are the most intensive producers of growth substances.
2. The treatment of seeds with suspensions of *Azotobacter chroococcum* stimulates the growth of seedlings, i. e. at the earlier stage of development, when the plant does not utilize the nitrogen from without.
3. Some other bacteria, which are not able to fix nitrogen when employed in peat preparations, produce a corresponding effect on plants in vessel experiments.

Below are adduced the experimental data, on the base of which we have made our conclusions.

1. Growth Substances Formation by *Azotobacter chroococcum* and Other Soil Bacteria. In the year 1931 Boysen-Jensen ([6]) found that of 17 investigated species of soil bacteria 13 produce growth substances of the auxin type. Among the bacteria examined by Boysen-Jensen one finds only few typical soil bacteria (*B. mycoides*, *B. subtilis*, *B. radiobacter*, *B. denitrificans*, *B. vulgatus*). We have studied the formation of growth substances by some soil bacteria on oat coleoptiles, the method of Boysen-Jensen was made use of. The results of the investigations are worthy of being more particularly exposed than it can be done in the present paper. Here we only give some conclusions (Table 1).

Table 1

The Production of Growth Substances by Different Soil Bacteria

Bacteria	The curvatures of the coleoptiles in degrees	Average value of oat coleoptiles curvatures
Mycobacterium rubrum	0; 0; 0; 0; 0;	0.0
Azotobacter vinelandii	0; 0; 0; 0; 0;	0.0
Bacillus mycoides	3; 2; 4; 5; 3;	3.4
Azotobacter agile	4; 9; 4; 7; 6;	6.0
Mycobacterium luteum	0; 3; 10; 10; 8;	7.0
Rhizobium leguminosarum	3, 7; 10; 13; 7;	8.0
Proteus vulgaris	16; 17; 13; 20; 0;	13.2
Bacillus subtilis	10; 17; 17; 20; 10;	14.8
Mycobacterium album	20; 18; 18; 10; 10;	15.2
Pseudomonas fluorescens	27; 17; 24; 18; 20;	21.2
Azotobacter chroococcum (str. A)	28; 28; 26; 22; 18;	24.4
Azotobacter chroococcum (str. 10A)	27; 24; 26; 37; 17;	26.2

As seen from the Table 1, of the bacteria investigated *Azotobacter chroococcum* belongs to the most intensive producers of growth substances. Nearly the same intensity of growth substance production is shown by *Pseudomonas fluorescens**. The intensity of growth substance production by other bacteria is much lower.

2. The Stimulation of Development in Seedings Treated with Suspensions of *Azotobacter chroococcum*. The seeds of flax were wetted either in water (control), or in a cell suspension of *Azotobacter chroococcum* (bacterized). Quartzy sand was used as mixer. To bacterize 100 seeds we have taken 0.3 cm^3 of the liquid containing about 500 millions of *Azotobacter cells* per 1 cm^3.

Two strains *of Azotobacter chroococcum* (A and 10A) were involved in the experiment. The strain A is used in the Institute of Agricultural Microbiology for azotogene preparations. After being wetted for 24 hours, the seeds were germinating on moist gauze in Koch's dishes. 7 days later a phytopathological test of the seedlings was made according to the instruction of the All-Union Institute of Flax ([7]), as well as the measurement of the height of the seedlings. The results are shown in Table 2.

As seen from cann Table 2, the seedlings treated with Azotobacter suspensions possess two peculiarities: they suffer less from attacks and grow more quickly.

* We cannot consider the bacteria which did not bend the coleoptiles, as not producing growth substances at all. They may produce a positive effect if the exposition is prolonged or a more sensitive variety of oats is used in the experiment.

Table 2

The Influence of Flax-Seed Treatment with *Azotobacter chroococcum* on the Development of Seedlings

Treatment of seeds	Sample of seeds	Germination ability p. c.	P. c. of diseased seedlings		Average size of the seedlings in cm
			Total	Heavily infected	
Control	364	93	53	—	8.60
Azotobacter chroococcum (str. A)	364	96	28	—	11.34
Control	148	96	75.5	11.5	4.05
Azotobacter chroococcum (str. A)	148	97	67.5	0	5.57
Control	148	98	83.5	8.5	5.97
Azotobacter chroococcum (str. A)	148	97.5	68.5	10.0	6.01
Azotobacter chroococcum (str. 10A)	148	98	54.0	1.0	6.48
Control	208	97	15.0	—	5.8
Azotobacter chroococcum (str. A)	208	98.5	5.0	—	7.2
Azotobacter chroococcum (str. 10A)	208	98.5	25.5(?)	—	7.7

Analogous experiments were carried out on wheat. To bacterize 105 grains, there were taken 1.5 cm^3 of the suspension, containing 500 millions Azotobacter cells per 1 cm^3. In 24 hours the wet seeds were sown in glass vessels filled with pure quartzy sand. The sand had been wetted up to 60% of its moisture capacity. 10 days later, the number of seedlings, the number of attacked and weakened plants and the total weight of 100 plants were determined. Besides, in one of the experiments, the control seeds were treated with peat and some other variants with azotogene (2 samples—«A» and «B»). The results are shown in Table 3.

Table 3

The Influence of Wheat-Grain Treatment with *Azotobacter chroococcum* on the Development of Seedlings

Treatment of seeds	Variety of seeds	Germination ability %	Total number of seedlings	Number of diseased seedlings	Weight of plants in g
Control	Ukrainka	95	89	8	4.13
Azotobacter chroococcum (str. A)		95	93	2	4.48
Azotobacter chroococcum (str. 10A)		97	96	4	4.59
Control	*Cesium* 0111	94	91	4	6.46
Azotobacter chroococcum (str. 10A)		95	92	4	6.74
Control	*Lutescens* 062	97	94	3	6.67
Azotogen («A»)		95	95	0	6.20
Azotogen («B»)		97	94	3	7.58

As may be seen from the Table 3, the treatment of wheat seeds with Azotobacter suspensions causes a growth acceleration in the seedlings and decreases the number of attacked plants. Azotogene «A» has shown no effect at all; azotogen «B» though accelerates the growth, yet does not decrease the number of affected plants*.

These results show that Azotobacter influences the growth of plants as early as in the seedling stage, i. e. when the nitrogen does not matter.

3. Peats Enriched by Some non Nitrogen-Fixing Bacteria Act as Azotogene. In 1937 an experiment on wheat (*Lutescens* 062) was carried out in small vessels, each containing 2.6 kg of soil (podzol). The soil was taken from the experimental field Dolgoprudnoje. The complete fertilizer consists of: superphosphate=1.24 g per vessel, KNO_3=0.4056 g; NH_4NO_3=0.3917 g; $CaCO_3$=2 g per 1 kg of absolutely dry soil. Wetted to 60% of its moisture capacity. The plan of the experiments was as follows: 1) dry seeds, 2) seeds moistened with water, 3) seeds mixed with pure peat, 4) seeds treated with peat and *Pseudomonas fluorescens* (strain B-17), 5) seeds treated with peat and *Pseudomonas fluorescens* (strain F-24), 6) seeds treated with peat and *Azotobacter chroococcum* (strain 10-A). Performed three times.

The experiment began on 27. V. 1937. The harvest was gathered on 20. VIII. 1937.

The results are shown in Table 4.

Table 4

The Influence of Seed Treatment with Non-Nitrogen-Fixing Bacteria and *Azotobacter chroococcum* on the Yield of Wheat

Treatment of seeds	Germination ability p. c.	The height of plants in cm			Yield in g per vessel			Yield in p. c. to control		
		8. VI.	19. VI.	1. VIII.	Grain	Straw	Roots	Grain	Straw	Roots
Control dry seeds	96	9.60	29.51	56.5	4.59	9.03	0.81	100	100	100
Control moistened seeds	96	13.26	28.29	57.06	4.36	8.84	0.72	94.8	97.9	96.5
Peat	94.6	13.66	28.62	56.50	3.74	7.48	0.70	81.5	82.9	85.5
Peat+*Pseudomonas fluorescens* (str. B-17)	100.0	13.13	27.61	59.06	5.69	8.64	0.92	123.9	95.7	105.7
Peat+*Pseudomonas fluorescens* (str. F-24)	98.5	12.39	28.37	55.80	5.74	8.80	1.12	125.0	97.5	108.4
Peat+*Azotobacter chroococcum*	97.5	12.88	28.34	59.06	5.37	8.05	0.73	116.9	89.2	103.2

As seen from the table, the peat treated with Azotobacter induces a yield increase of 16.9%, while the same peat treated with non nitrogen fixing bacteria gave an increase of 23.9 and 25.9%. The plants treated with *Azotobacter chroococcum* and *Pseudomonas fluorescens* (strains B-17) were at first shorter than the controls, but beginning from 1. VII. 1937, they grew higher than the latter.

This experiment is the more interesting as in spite of the plants having been provided with nitrogen, the azotogene has produced the same effect.

* If badly infected seeds are treated with Azotobacter the effect is not positive but even a negative one.

Analogous results were obtained in a vessel experiment of flax-variety =0107. The total infection is 2%, germination ability is 98.5%. Virgin soil. The vessels were provided with a complete fertilizer (NPK). Performed three times. Sowing on 10.VI.1937. Harvesting on 28. VIII.1937. Control seeds treated with moistened peat. The seeds were bacterized with suspensions of different bacteria (*Azotobacter chroococcum*, *Pseudomonas fluorescens*). The results are shown in Table 5.

Table 5

The Influence of Seed Treatment with Non-Nitrogen-Fixing Bacteria and *Azotobacter chroococcum* on the Yield of Flax

Treatment of seeds	Germination ability p. c.	The height of plants in cm			Yield in g per vessel		Yield in p. c. to control	
		9. VII.	20. VII.	28. VIII.	Seeds	Straw	Seeds	Straw
Control	97.3	35.9	75.4	113.2	5.06	22.55	100	100
Pseudomonas fluorescens (str. B-17)	96.5	38.0	76.0	111.8	5.73	22.41	113.2	99.4
Pseudomonas fluorescens (str. F-24)	95.8	37.0	80.4	116.8	5.37	24.23	106.3	107.5
Azotobacter chroococcum	95.2	36.0	73.6	116.1	6.06	22.1	119.7	98.0

As seen from the Table 5 Azotobacter produces the same effect as the other bacteria which are unable to fix nitrogen.

4. Conclusions. The assumption that azotogene increases the yield owing to nitrogen fixing activity of Azotobacter, is possible, but lacking further evidence. To form an idea of the nature of the action of azotogene it is necessary to take into account the stimulating effect of Azotobacter on higher plants.

The statement advanced in the present notice may be of high importance for the practice of manufacturing of azotogene (and other bacterial preparations of fertilizers).

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PLANT PHYSIOLOGY

PERMEABILITY OF PLASMA AS A FACTOR OF RESISTANCE TO COLD

By B. M. GOLUŠ

(Communicated by A. A. Richter, Member of the Academy, 31. XII. 1937)

We have established in our previous works (1) that it is possible to judge about the resistance of cereals to cold from the permeability of their protoplasm. In freezing wheat and rye varieties, of different winter-hardiness, we have established that there is no equal increase in the permeability of their plasma, the increase being the lower, the more cold-resistant is the variety. Having found this method to be valid for cereals we set ourself the task to check it on other crops.

The aim of the present work was to check our method on peas. S. M. Ivanov (2) studied the cold-resistance of different pea varieties by the direct method of freezing. For our research we chose the pea varieties different as to their cold-resistance (after S. M. Ivanov). Cold-resistant peas were represented by the Zolotoi 1769 and Peas 3452, while the non-resistant by the Sibirskij 961, Zakavkazskij 2367 and Arkhangelskij 1529. The plants were grown in a hothouse at +18, +19°C. We worked after the same method, as had been applied to our previous research. Only one gram of leaves was taken for analysis, instead of two taken in studying cereals.

Freezing was carried on in 2 criohydrates: $S2(NO_3)_2$ — 5.75° and $BaCl_2$ —7°.8 C with two expositions—during two and four hours.

The data relating to the freezing of Peas 1769 at a temperature of — 5.75°C are arranged in Table 1.

The relative data have been derived from comparison with the control, the permeability of the latter being assumed to be equal to unity.

As is seen from the table, the permeability of the plasma increases with the time of exposure.

Table 2 gives the respective data for the variety Zolotoi 1769 exposed to frost at — 7.8°C.

From these two tables it may be seen that the permeability of plasma is the greater the longer the exposure and the lower the temperature.

Same regularities have been revealed in the experiment with non-resistant peas Sibirskij 961 (Table 3 and 4). If we compare these tables to the preceeding ones we may note the same influence produced by the temperature and time of exposure upon the colloidal state of the plasma changing its permeability. Peas 961 which has been classed by S. M. Ivanov (2) among non resistant varieties, is according to our experiment, more hardy than 1769. This may be explained by the fact that the pea 1769 enjoys no stable place in Ivanov's classification, being the first among hardy varieties, or the last

Table 1

Changes of Permeability of the Plasma in Peas Zolotoi 1769 Exposed to Frost at —5°.75 C

Date of experiment	Permeability of plasma in control plants	Permeability of plasma in plants exposed to frost during 2 hours		4 hours	
		Absolute data	Relative increase	Absolute data	Relative increase
25.XII.	4, 3 } 3.5	63, 61 } 62	17.7	71, 68 } 69.5	19.8
29.XII.	5, 3 } 4	66, 59 } 62.5	15.6	73, 71 } 72	18
3.I.	7, 3 } 5	55, 60 } 57.5	11.5	62	12.4
9.I.	5, 6 } 5.5	55, 58 } 56.5	10.2	—	—
10.I.	6, 7 } 6.5	58, 66 } 62	9.5	83, 81 } 82	12.6
13.I.	5, 7 } 6	56, 60 } 58	9.8	62, 61 } 61.5	10.2

but one among the medium resistant ones alternatively. Evidently this variety requires additional study.

In Table 5 the data on permeability of three pea varieties are brought together.

Table 2

Changes of Permeability of the Plasma in Peas Zolotoi 1769 Exposed to Frost at —7°.8 C

Date of experiment	Permeability of plasma in control plants	Permeability of plasma in plants exposed to frost during 2 hours		4 hours	
		Absolute data	Relative increase	Absolute data	Relative increase
15.XII.	6, 5 } 5.5	79, 84 } 81.5	14.8	89, 97 } 93	16.9
17.XII.	7, 6 } 6.5	83, 89 } 86	13.2	94, 98 } 96	14.0
19.XII.	4, 5 } 4.5	79, 82 } 80.5	17.0	89, 87 } 88	19.5
21.XII.	4, 5 } 4.5	84, 86 } 85	18.0	92, 91 } 91.5	20.3
23.XII.	6, 7 } 6.5	65, 75 } 70	10.7	—	—
14.I.	5	71	14.2	79, 82 } 80.5	16.1

As is seen from the tabulated data, the most resistant are the Peas 3452; the remaining 2 varieties are less resistant. Examining the results obtained one can arrange the varieties in the following series, according to the descend-

Table 3

Change in Permeability of the Plasma of Peas Sibirskij 961 Exposed to Frost at —5°.75 C

Date of experiment	Permeability of plasma in control plants	Permeability of plasma in plants exposed to frost during 2 hours		4 hours	
		Absolute data	Relative increase	Absolute data	Relative increase
25.XII.	9, 11 } 10	96, 93 } 94.5	9.4	100, 98 } 99	9.9
26.XII.	11, 10 } 10.5	—	—	118	10.2
27.XII.	8, 9 } 8.5	90, 88 } 89	10.4	94, 94 } 94	11.0
29.XII.	7, 9 } 8	92, 94 } 93	11.6	101, 98 } 99.5	12.4
31.XII.	7, 10 } 8.5	94, 96 } 95	10.1	99, 98 } 98.5	11.5
3.I.	6, 8 } 7	77, 82 } 79.5	11.3	86	12.2
5.I.	8, 9 } 8.5	75, 81 } 78	9.1	83	9.7
10.I.	9, 12 } 10.5	99, 102 } 100.5	9.5	98, 106 } 102	9.7

ing degree of their resistance to cold (after the results obtained with —7°.8 temperature and 4-hour exposure).

1. Peas 3452.
2. Zakavkazskij 2367.
3. Sibirskij 961
4. Zolotoi 1769.
5. Arkhangelskij 1529.

Table 4

Change in Permeability of the Plasma in Peas Sibirskij 961 Exposed to Frost at —7°.8 C

Date of experiment	Permeability of plasma in control plants	Permeability of plasma in plants exposed to frost during 2 hours		4 hours	
		Absolute data	Relative increase	Absolute data	Relative increase
15.XII.	7, 12 } 9.5	117, 114 } 115.5	12.1	124, 122 } 123	12.9
17.XII.	8, 9 } 8.5	128, 125 } 126.5	14.8	131, 131 } 131	15.4
19.XII.	6, 11 } 8.5	119, 121 } 120	14.0	125, 122 } 126	14.8
21.XII.	7, 10 } 8.5	126, 130 } 128	15.0	134, 133 } 133.5	15.7

Table 5

Change in the Permeability of Plasma in Different Varieties of Peas Exposed to Frost at —7.8° C

Date of experiment	Variety	Permeability of plasma in control plants	Permeability of plasma in plants exposed to frost during			
			2 hours		4 hours	
			Absolute data	Relative increase	Absolute data	Relative increase
26.I.	Peas 3452 (resistant) .	7, 9 } 8	64, 74 } 69	8.6	68, 71 } 69.5	8.7
28.I.	» 3452 » .	7, 8 } 7.5	45, 50 } 47.5	6.3	65, 60 } 62.5	8.3
10.II.	Peas Arkhangelskij 1529 (non resistant) . . .	5, 7 } 6	58, 66 } 62	10.3	101, 99 } 100	16.7
16.II.	Peas Arkhangelskij 1529 (non resistant) . . .	4, 6 } 5	61	12.2	107, 102 } 104.5	20.9
10.II.	Peas Zakavkazskij 2367 (non-resistant) . . .	7, 8 } 7.5	72, 71 } 71.5	9.5	106, 100 } 103	13.7
16.II.	Peas Zakavkazskij 2367 (non-resistant) . . .	8, 9 } 8.5	76, 80 } 78	9.2	108, 116 } 112	13.2

This coincides with Ivanov's data in substance. Following conclusion may be drawn from our research:

1. The experiments carried out with pea varieties very different as to their cold resistance fully confirm the statements set forth in our previous papers on cereals.

2. The results of the experiment authorize us to state that the factor of permeability of the plasma should be taken into account among other factors when testing crops for their cold resistance.

3. In the present case, as well as in that of cereals the results generally coincide with the classification based on the direct method of freezing.

4. The method of estimating the permeability of plasma described in this notice is simple, if compared to others and, a great amount of material can be shortly analyzed when using it.

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PLANT PHYSIOLOGY

DIFFERENTIAL NUTRITION OF THE SUNFLOWER WITH PRINCIPAL ELEMENTS

By T. DEMIDENKO

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The sunflower belongs to that class of agricultural plants whose root feeding has been studied very little, in spite of the high economic value of this crop.

In the inflow of nutrient elements to the root of a plant we observe, as it seems, a definite sequence similar to that of the thermal and light stages, discovered by Academician Lysenko [8] in the general development of the plant. This sequence has not yet been established, though it forms a part in the general cycle of the development of the plant since sowing till complete ripeness [1–7].

If in the nearest future the experimenters could establish or discover those periods in which the plant has to be given a maximum resp. minimum quantity of nutrient substances, we would obtain higher crop yields by regulating other factors of growth in their optimal relations. Unless we possess a worked out plan for artificial feeding each crop at definite periods, the use of fertilizers in practical farming would not be sufficiently effective.

A detailed study of this question may be achieved by growing plants in water and eliminating individual nutrient elements or their combinations approximately every 5—10 days. In that case we may obtain comparatively clear and stable results, on the basis of which we can build a definite system of fertilization in order to use most efficiently the nutrient substances introduced into the soil.

The present investigation purposed to establish, on the basis of artificial nutrition used in practical farming, the absorption of the leading elements (N, P, K) by the sunflower within very narrow time limits.

The nutrient mixture of Tsintsadze with 5.5—5.6 pH, which according to our observations is the most favorable for the development and growth of the sunflower, was chosen by us for the experiments. The supply of N, P, K was cut off four times during the summer, at the time when under the conditions of practical farming it was quite harmless to introduce artificial feeding.

The results and the scheme of the experiments are tabulated below.

From these data we may draw the following conclusions:

1. If the sunflower grown in water cultures is deprived of nitrogen before the head has begun to form, when it is forming completely, during and at the end of flowering, during the formation of seed—the yield is comparatively high. This is explained by the fact that this element is absorbed by the plant before milk ripeness. It is used for the formation of the kernel which consists of a considerable amount of protein compounds.

2. The greatest amount of nitrogen is absorbed by the sunflower before

Vessels	Scheme of the experiments	Yield of dry substance	Crop yield		Discharged by the plant		
			in g	in p.c.	N	P_2O_5	K_2O
1— 4	Normal mixture	80.48	19.74	100.0	1.2072	0.1775	3.6793
5— 8	Without nitrogen (beginning of head formation)	67.48	17.38	82.97	0.8622	0.1686	4.2375
9—12	Without nitrogen (head formation)	69.37	19.56	99.08	1.0405	0.1594	4.0431
13—16	Without nitrogen (flowering)	72.48	20.55	104.10	1.0872	0.1442	3.7365
17—20	Without nitrogen (seed formation)	76.44	20.96	106.18	1.1466	0.1237	3.7035
21—24	Without phosphorus (beginning of head formation) .	94.37	23.35	118.2	1.4155	0.1719	3.7673
25—28	Without phosphorus (head formation)	90.54	22.18	112.3	1.3581	0.1811	4.3640
29—32	Without phosphorus (flowering)	82.32	21.32	108.0	1.2348	0.1991	4.5486
33—36	Without phosphorus (seed formation)	78.16	19.75	100.00	1.1724	0.2076	4.7237
37—40	Without potassium (beginning of head formation) .	72.37	18.34	92.9	1.0855	0.1592	3.4882
41—44	Without potassium (head formation)	96.32	23.54	119.2	1.4448	0.1637	4.6426
45—48	Without potassium (flowering)	105.46	24.33	123.2	1.5819	0.1835	5.0831
49—52	Without potassium (seed formation)	106.35	20.75	105.1	8.5952	0.2244	5.1260

flowering, during an intensive formation of the stem and leaves, at the expence of the assimilants and products formed of carbohydrates and nitrogen.

3. Though the sunflower absorbs a considerable amount of phosphoric acid during vegetation, it stores up this element mostly before the formation of head.

4. The sunflower intensively absorbs considerable amounts of potassium during photosynthesis, i. e. before flowering, when it takes an active part in the transportation of carbohydrates and their migration from the leaf to the storing points.

5. There is no regular utilization by the plant of these three elements, when they are introduced into the soil at definite periods or when normal salines are eliminated. The smaller was the amount of nitrogen, phosphorus and potassium, the more rational was their distribution in the synthesis of the unit of the productive substance.

6. The longer are the plants kept on a normal nutrient substance, the greater is the amount of the substances absorbed during the period of vegetation; the plant stores them in a quantity above the normal.

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PLANT PHYSIOLOGY

DIFFERENTIATED NUTRITION OF SUGAR BEET WITH PRINCIPAL ELEMENTS

By V. P. POPOV

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The vegetable cell is a physico-chemical structural system built of organic substances—electrolytes and ensymes which are in definite condition and definite relation to each other. It is characterized by the course of the processes, which have the same trend as in microheterogeneous systems, surface phenomena, moreover, being of exceptional importance.

The transformation of the static in itself vegetable colloid system, into a dynamic one depends both on the chemical substrate of the system on which the processes occur and on the fact that besides the organic colloids—proteins, phosphatides, sterins and carbohydrates—electrolytes too, enter into the composition of the system ([4]).

The high mobility of the electrolytes, their bio-dynamic ability, determines the course of the processes of metabolism within a vegetable cell and creates new structures which are both a plastic material, and a source of energy for the organism. This renders necessary the study of their influence upon the whole vegetable organism ([2, 4, 5, 7]).

The presence of electrolytes in the nutritive solution, their concentration at one or another period of plant development influence the colloid-chemical composition of the plant in the course of growth ([1—7]).

Among the other elements of root nutrition P and K play an exceptional part and their presence in the nutritive solution during definite phases of plant development lays its imprint on the whole subsequent vegetation, the entire carbohydrate-colloid complex, the structure and properties of the plasma, in particular, on the hydrophility of the latter ([1—3, 6—13]).

The question should be examined concerning the terms of suppling the plant with P and K, since the presence or the absence of any electrolyte in the solution during a certain phase of plant development essentially influences the yield and chemical composition ([1—3, 7—12]).

The biochemical cycle of the plant's development can be directed towards the accumulation of profitable characters, if we timely supply the plant with nutritive substances, and precisely with those it requires at the given moment.

Sugar beet is particularly succeptible to changes in conditions of growing, to the presence of elements of root nutrition. Therefore, the problem of supplying the sugar beet with N, P and K in definite periods is studied,

under the aspect of a physiological interpretation of data on supplementary feeding obtained in practical agriculture ([1–3, 7–12]).

For studying the changes occurring in the plant under the influence of each one of the elements the following methods may be applied: either the direct introduction of the element into the nutritive solution at a definite stage of development, or its elimination from the nutritive mixture.

This enables to establish the response of the plant to the action of element under investigation and the periods of maximum consumption of the basic nutritive substances.

The present work represents the result of such a research carried out on water cultures.

Beloussov's nutritive mixture was used, which for the separate study of P and K was modified; P being introduced as Ca $(H_2PO_4)_2$, and K as KCl, according to the rates of the original mixture.

The plants were supplied with a complete nutritive mixture till a definite stage of development, then the element tested (N, P, or K) was eliminated and they received the mixture, deprived of this element until the end of vegetation

These are the stages when the elements were eliminated:

1st — 6 pairs of comletely developed leaves
2nd — 8 » » » » »
3rd — 10 » » » » »
4th — 13 » » » » »

The results are shown in the following Table:

Elimination N, P and K

Nutritive mixture and stage of development	Weight of root		Sugar content %	Coefficient of colloidality K	Viscosity η	Surface tension	Content in the root	
	g	%					Total N	P_2O_5
Control								
Original mixture	311	100	19.6	5.42	2.168	67.5	1.1387	0.7714
without N: 6 pairs of leaves	229	73.6	19.7	7.38	2.154	73.4	0.3453	0.8714
without N: 8 » » »	280	90.0	18.9	7.28	2.585	72.7	0.5070	0.8025
without N: 10 » » »	285	91.6	18.0	6.32	2.593	72.5	0.7636	0.7701
without N: 13 » » »	308	99.0	17.1	6.30	3.121	67.7	1.0420	0.7094
Control								
Modified mixture	319	100	17.8	5.50	2.245	64.5	0.8987	0.7795
without P: 6 pairs of leaves	217	68.0	15.4	7.64	2.629	59.8	1.4152	0.4951
without P: 8 » » »	220	68.9	15.5	7.25	1.921	61.3	0.7935	0.5660
without P: 10 » » »	243	76.1	16.2	6.98	1.707	65.6	0.7922	0.6232
without P: 13 » » »	259	81.1	17.5	6.63	1.696	71.4	0.7707	0.7817
without K: 6 pairs of leaves	132	41.4	14.5	7.20	1.606	69.9	1.3500	1.0734
without K: 8 » » »	191	59.8	15.5	7.44	1.799	68.3	0.9158	0.8199
without K: 10 » » »	199	62.3	17.0	8.52	1.906	65.0	0.8397	0.8636
without K: 13 » » »	250	78.4	17.5	11.98	2.228	58.2	0.8381	0.8347

The earlier the beet is deprived of nitrogen nutrition, the lower is the yield of root.

When N is eliminated at the stage of 6 pairs of leaves the weight of the root equals 229 g of N, or 73.6 p. c. while, at the stage of 8.10 pairs of leaves, the plant has stored up nitrogen necessary for forming the plant organism, and the yield reaches 90—91. 6 p. c. of the control.

Thus, for the normal development of beet, nitrogen is mostly required at its young age, when the basis of the plant organism, and the assimilating surface are being created.

The consumption of phosphorus is more regular and when P is eliminated by the time of the development of 8 pairs of leaves, the weight of the root at that time does not surpass 68.9 p. c.

Potassium is efficient at latter dates and its elimination, at the time of 10—13 pairs of leaves results in a yield of 62.3 to 78.4 p. c.

The sugar content of the beet decrease the more the later nitrogen is eliminated. For the elimination of nitrogen at the time of 6 and 13 pairs of leaves, the figures of sugar content are 19.7% on 17.1% respectively.

The influence of phosphorus and potassium on the sugar content is directly opposite to that of nitrogen: the longer the beet is fed with phosphate or potassium the higher its sugar content.

The elimination of P at the time of 6 and 13 pairs of leaves brings about a 15.4% and 17.5% sugar content respectively.

Potassium is still more efficient. The sugar content rises from 14.5% to 17.5% if one prolongs the feeding of beet with K to later dates.

The elimination of nitrogen leads to a decrease of the colloidality of beet, which is the more marked, the later nitrogen is eliminated. 7.38 and 6.30 are the values of the coefficient of colloidality for the first and the fourth period respectively.

In experiments with sand cultures, where nitrogen was introduced into the nutritive mixture, a continuous increase of the colloidality of beet was obtained.

Thus we arrive at the conclusion that nitrogen promotes the formation of hydrophile colloids in the sugar beet.

The same is true with respect to phosphorus, yet the influence of the latter is not so strong. When P is eliminated at the 6-pairs-of-leaves period, the coefficient of colloidality amounts to 7.64; whereas in a beet deprived of P at the period of 10 pairs of leaves, it equals 6.63.

The elimination of potassium from the nutrition at the early age (6 pairs of leaves) gives a coefficient of colloidality equal to 7.20, while a sharp increase, up to 11.98, is recorded if K is eliminated at the second half of the vegetation period.

Direct introduction of potassium at this time results in a noticeable decrease of beet colloidality.

Thus, potassium exerts a depressive influence on the accumulation of colloids in beets.

As regards viscosity of the cell juice of beets we note:

1) The later the beet is deprived of N nutrition, the higher is the viscosity, amounting to 3.121 in the fourth period.

The same dependence is recorded in the experiments with potassium.

2) The later the beet is deprived of phosphate nutrition, the lower is the viscosity of the juice.

With the decrease of juice viscosity the surface tension increases.

Analysis of ash elements indicates that at a young age the accumulation of N in the root is not considerable (0.3458—0.5070 p. c.), it being used up in the development of the assimilating system; only in the later period, it accumulates in the root intensively.

Whereas the accumulation of phosphorus in the root of a young beet is sufficient. The most noticeable is the antagonism between P and N in the experiments with nitrogen.

The elimination of phosphate from nutrition results in small changes in the content of N, but the amount of P_2O_5 absorbed by the plant is changed considerably.

Thus, when P is eliminated from the nutrition of a beet with 6 pairs of leaves, the content of P_2O_5 equals 0.4951 p. c.; whereas, in the case of a beet with 13 pairs of leaves, the per cent of P_2O_5 is 0. 7817.

The elimination of potassium decreases the rate of accumulation of the other two elements in the plant.

Conclusions

1. a) Nitrogen promotes the accumulation of hydrophile colloids in sugar beet.

b) Phosphorus acts in the same way, but is not so efficient.

c) In the second half of vegetation, potassium depresses the accumulation of hydrophile colloids in the beet.

2. The later the beet is deprived of nitrogen and potassium nutrition the higher is the viscosity of the juice.

Phosphorus acts in the reverse direction.

3. Nitrogen is most efficiently utilized at the early stage of the beet growth, whereas potassium, in the second half of vegetation.

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PALÉONTOLOGIE

DE LA FAUNE PALÉOCÈNE DE MOLLUSQUES TROUVÉE AU CAUCASE DU NORD

Par I. A. KOROBKOV

(Présenté par A. A. Borissiak, de l'Académie, le 2. XII. 1937)

Dans les régions occidentales du Caucase du Nord entre les roches flyches claires du Crétacé supérieur et les dépots foncés sablo-argileux du niveau Goriatschy Klutsch se trouvent des gisements d'une suite de roches flyches qui portent le nom de niveau Tsitsé *. Ce nom a été proposé par N. B. Vassoevitch (*) au lieu de celui de «flyche éocène». Le niveau Tsitse est caractérisé par l'alternance de marnes compactes vert ou gris-verdâtre, parfois sonores, avec de minces intercalations de grès calcaires serrés à grains menus et moyens; parmis ces grès on trouve fréquemment des variétés à stratification onduleuse. Non moins souvent on y rencontre des grès à grains grossiers, des intercalations d'agglomérats argileux et des enclaves de roches crétacées. Le caractère lithologique et la puissance du niveau Tsitse ne sont pas constants. Fréquemment on observe même à une courte distance de brusques modifications de ce niveau, ainsi que des modifications dans la lithologie des intercalations, qui séparent les marnes vertes.

A l'est, dans les régions des rivières Selentchouki, Couban, Couma, Daria et Podkoumka, c'est le niveau elbourgien, exclusivement marneux, établi par K. A. Prokopov, qui correspond sous le rapport stratigraphique au niveau Tsitsé; or à l'ouest, dans la région d'Anapa, c'est le niveau littoral également établi par K. A. Prokopov et caractérisé par l'alternance de grès serrés, souvent à stratification onduleuse, avec des grès friables et des marnes schistoïdes gris foncé. L'âge du niveau Tsitsé n'est pas déterminé. Certains investigateurs rapportent ce niveau à l'étage danien et d'autres au paléocène. Jusqu'en 1936 on n'avait pas découvert d'organismes fossiles dans les roches du niveau Tsitse, excepté les foraminifères qui ont été étudiés par B. M. Keller.

Notant le changement excessivement brusque qu'on observe dans les espèces composant la microfaune et surtout le plankton lors de la transition des dépôts maestrichtien au niveau Tsitsé, B. M. Keller (1) rapporte l'âge de ce dernier au danien. Se basant sur l'étude de la microfaune N. N. Soubotina (2) rapporte à l'étage danien le niveau elbourgien—l'équivalent indiscutable du niveau Tsitsé dans les régions situées vers l'est. B. M. Keller et N. N. Soubotina étant d'accord sur l'âge du niveau Tsitsé et du niveau el-

* Dans la région de Neftiano-Schirvansk les analogues du niveau Tsitsé ont été nommés par S. T. Korotkov(3) — série de Touchinsk.

bourgien, diffèrent absolument quant à la question de l'âge du niveau Goriatschy Klutsch qui recouvre directement les dépôts indiqués. Le premier de ces investigateurs dont l'opinion est confirmée par les données de M. A. Glessner*, rapporte le niveau Goriatschy Klutsch au paléocène tandis que le second le rapporte à l'étage danien. Cette divergence d'opinions nous amène sans doute à une construction de systèmes paléographiques contradictoire ainsi qu'à des conclusions qui se contredisent en ce qui concerne le volume et la subdivision de l'étage danien dans le Caucase du Nord.

En 1936 le géologue du trust «Mayneft» N. I. Kiyko fit la découverte d'uné faune de mollusques dans les roches de la partie supérieure du niveau Tsitse, région d'Ilsk. L'année suivante le géologue du même trust A. A. Chmelev trouva également une faune de mollusques au même niveau dans la région d'Azov qui est limitrophe de la précédente dans la direction de l'est. Pendant l'été 1937 je recoltai cette faune dans les lieux indiqués et j'en entrepris l'analyse. La note présente est un exposé sommaire des résultats de cette étude.

Dans la région d'Ilsk une faune de mollusques a été trouvée dans une marne compacte verdâtre, non stratifiée d'une épaisseur de 0.03—0.06 m avec des taches noires dendroïdes, et gisant dans la partie supérieure du niveau Tsitsé près du contact avec les roches qui forment la transition au niveau Goriatschy Klutsch. Les marnes contiennent de petites enclaves de roches crétacées, des galets appartenant aux couches inférieures du niveau Tsitsé, des débris d'ammonites et de menus fragments de la couche prismatique d'inocérames.

Dans la région d'Azov une faune de mollusques plus riche en espèces différentes a été trouvée dans les couches d'un agglomérat argileux gisant dans le toit du niveau Tsitse. Toutes les sept couches de cet agglomérat contiennent une faune et sont séparées l'une de l'autre par des couches intermédiaires de grès fins et par des argiles calcaires noires et verdâtres. L'épaisseur globale de la stratification des agglomérats est de 28 à 29 m.

Les coquilles des mollusques des deux gîtes n'ont aucun indice qui fasse supposer qu'elles aient été roulées, ce qui, de même que la présence de valves à parois très minces, témoigne qu'elles ont été trouvées in situ.

L'étude de la faune récoltée m'a permis de déterminer les espèces suivantes:

1. *Solenomya pavlovi* (Arkh).
2. *Corbis korotkovi* Korobkov.
3. *Variamussium* cf. *clipeolum* Korobkov.
4. *Athleta (Volutospina) elevata* (Sow.).
5. *Turritella* cf. *circundata* Desh.
6. *Actaeonidea (Crenilabium) elata* (Koenen).
7. *Dentalium* sp. (cf. *rugiferum* Koenen).

Mollusques dont l'espèce n'a pu être établie:

1. *Nucula* sp.
2. *Ammusium* sp. *(Occultamussium)* sp.
3. *Natica* sp.
4. *Bullinella* sp.
5. *Roxonia*, sp.

Nouvelles especes établies:

1. *Nuculana ciceensis* n. sp.
2. *Corbis korotkovi* Korobk. var. *edecimata* n. var.

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* Ces données sont tirées de l'ouvrage de B. M. Keller (1), p. 641, note.

Parmi les espèces déterminées les espèces suivantes sont communes au niveau Tsitsé et au paléocène du Volga:

1. *Solenomya pavlovi* (Arkh.).
2. *Athleta (Volutospina) elevata* (Sow.).
3. *Turritella* cf. *circundata* Desh.
4. *Actaeonidea (Crinilabium) elata* (Koenen).
5. *Dentalium* sp. *(cf. rugiferum* Koenen).

Espèces communes au niveau Tsitse et au niveau elbourgien:

1. *Solenomya pavlovi* (Arkh.).
2. *Variamussium* cf. *clipeolum* Korobkov.
3. *Athleta (Volutospina) elevata* (Sow.).
4. *Actaeonidea (Crenilabium) elata* (Koenen).
5. *Dentalium* sp. (cf. *rugiferum* Koenen).
6. *Natica* sp.

Il est à noter que l'espèce *Corbis korotkovi* Korobk. a été trouvée auparavant dans les dépôts supérieurs jusqu'à l'oligocène inférieur.

Il ne suffit pas de pouvoir énumérer les espèces pour arriver à une conclusion positive à l'égard de l'âge, toutefois la présence de cinq espèces communes au paléocène du Volga, dont deux (*Athleta elevata* Sow. et *Actaeonidea elata* Koenen) sont communes au paléocène danien ([3], [4]), permet de conclure que le paléocène est l'âge le plus probable du niveau Tsitsé. La présence dans le complexe étudié de six espèces, communes au niveau Tsitsé et au niveau elbourgien confirme une fois de plus le synchronisme de ces deux niveaux. La faune de mollusques du niveau elbourgien riche en espèces n'a pas encore été suffisamment étudiée, mais une analyse préalable a manifesté un manque total d'espèces crétacées et daniennes et la présence de huit espèces paléocènes, dont six sont communes au paléocène danien.

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